THERMODYNAMICS

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FOR STUDENTS OF CHEMISTRY

BY

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WITH ELEVEN DIAGRAMS

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PREFACE

THIS book has been developed from lectures in which I have done what I can to make the fundamental ideas of thermodynamics as clear as possible, and particularly to explain the methods by which the abstract general laws are brought to bear upon the actual problems of physics and chemistry By the degree in which this one object is attained the book must be adjudged successful or otherwise It seeks to contribute something to the clearing up of those difficulties in understanding the principles of an unfamiliar subject which most students of chemistry experience, and I have tried throughout to discuss in some detail precisely those points which I know to be found difficult

There is no advantage in presenting a formally unified system, because the laws of thermodynamics can be clothed in many forms, choice between which is entirely a matter of individual preference or of circumstances, and nobody can be at home with original literature without some acquaintance with them all I have tried, therefore, to exemplify a number of the more important methods

A good deal of stress is laid, all through the book, on the interconnection between the laws of thermodynamics and the kinetic theory This is in a sense a departure from a rigid thermodynamic method, but I think the gain in clearness is very great I am out of sympathy with those who regard thermodynamics as a science based upon empirical laws independent of the actual nature of things If it were not for the molecular-kinetic nature of things there is no particular reason for believing that the laws of thermodynamics would be what they are

C N H

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THERMODYNAMICS FOR STUDENTS OF CHEMISTRY

CHAPTER I

INTRODUCTORY

THE AIM OF THERMODYNAMICS IN CHEMISTRY

IN the earlier stages of its development chemistry dealt almost exclusively with the transformations of matter The properties and composition of substances were studied and the means by which these substances might be converted into others of different properties were investigated. But when interest became directed to the actual process of chemical change, and when the mechanism of the transformations as well as the properties of the various products was studied, it was necessary to take into account not only material changes but also accompanying energy changes

All natural processes are associated with energy changes which play an essential rôle in the phenomena In problems of mechanics the relations of matter and energy are clear and distinct If we have, for example, a smooth and perfectly elastic sphere of mass m, moving with velocity u, it has in virtue of its motion a kinetic energy $\frac{1}{2}mu^2$, because this amount of work would have to be done on it in order to bring it to rest If it now impinges directly upon a second smooth and perfectly elastic sphere of the same mass it will be brought to rest, while the second sphere will move off with velocity u, and therefore with kinetic energy $\frac{1}{2}mu^2$. That is to say an amount of kinetic energy $\frac{1}{2}mu^2$ has been transferred from the first sphere to the second, while no actual material change has taken place In this case the energy change is not only the essential but the sole feature of the process

In the more complex phenomena of physics and chemistry the relations are necessarily more involved and difficult to picture. Material changes and energy changes occur simultaneously For instance all the material changes of chemistry are accompanied by evolution or absorption of heat, and these heat changes represent a very essential part of the phenomenon. The problem therefore presents itself in what ways does the heat change govern the chemical reaction? Or if we consider the processes of vaporisation and fusion we find that both are accompanied by the absorption of heat, and a similar problem arises concerning the connection between the heat changes and the phenomena of change of state We know, for example, that the boiling point of a liquid is dependent on the external pressure, and we might enquire whether the extent of this dependence is connected in any way with the latent heat of vaporisation. Questions of this sort all involve the consideration of rather subtle interrelations of matter and energy Two main roads of attack are open , one through the kinetic theory of matter, the other through the laws of thermodynamics The laws of thermodynamics are closely and fundamentally connected with the kinetic theory of matter but are more general in their application

THE KINETIC THEORY OF MATTER, AND THE DYNAMICAL THEORY OF HEAT

The most cursory survey of natural phenomena suffices to show that heat changes play a unique part in nature They accompany nearly every natural process—the expansion of a gas, the stretching of a soap film, chemical union or decomposition, vaporisation and fusion

This is a consequence of the molecular nature of matter and the fact that heat is a manifestation of the irregular motion of the molecules of a body After outlining briefly the kinetic theory we may illustrate this point by a few examples

The evidence that matter is molecular in nature is primarily chemical. The laws of constant and multiple proportions lead one to infer that matter is made up of discrete structural units, and the recent work of Perrin on colloidal solutions has placed the question of the real existence of molecules beyond dispute

Considering first a gas as the simplest case, the total volume of the gas must be large compared with the actual space occupied by the molecules, since the same number of molecules merely by moving closer together when the gas liquefies pass into a volume many hundreds of times smaller When, for example, 1 c c. of water vaporises and gives 1,750 c cs of steam the same number of molecules are scattered through a volume 1,750 as great, and the distances between them must be very great compared with their proper magnitudes

The molecules of a gas are not at rest but moving in all directions, and continually colliding with one another The direction of the line of centres and the relative velocities of two molecules at the moment of an impact may vary almost indefinitely from case to case, so that the velocity of a given molecule may be changed as the result of a collision from almost any value to almost any other As a result of several successive impacts of a favourable kind the molecule can acquire a very great velocity, or on the other hand may be brought nearly to rest

Among the millions of molecules contained in a cubic centimetre of gas at atmospheric pressure it is impossible practically to trace out the history of the changes in velocity of a single molecule due to its successive impacts, but it is clear that on the average certain types of event are much more likely to occur than others For instance, though it is possible for a single molecule to acquire an enormous velocity as the result of a long series of impacts of a special type, it is very improbable that a long series of these favourable impacts will occur without the occurrence of unfavourable impacts, i e impacts resulting in a diminution of velocity It follows, therefore, that, on the average, out of a very large number of molecules the proportion which acquire this great velocity will be small Actually the velocity of a single molecule rises and falls about a mean value, rising only rarely to a very high value when a succession of favourable impacts have occurred, and falling only rarely to a value near zero when a succession of ' unfavourable ' impacts have occurred

The various states assumed by a single molecule over a long series of collisions are reproduced simultaneously when a great number of molecules are taken together at a given instant A certain proportion have very large velocities, some have very low velocities The velocities are said to be ' distributed ' about a mean value The velocity of a single molecule varies continually, but when many millions of molecules are considered the fraction of the total number which have velocities between certain specified limits is practically constant This state of affairs is known as a statistical distribution

The velocity, c, of a molecule is determined in magnitude and direction when three rectangular components, u, v, w, are known, such that $c^2 = u^2 + v^2 + w^2$

The number of molecules possessing velocity components between u and $u+du$ is given by the expression $A \; {}^{-u^2/\alpha^2} du$, where A and α are constants

This is known as Maxwell's distribution law.

If a mass of gas is unconfined by a containing vessel, those molecules on the outskirts which happen to possess velocities directed away from the centre of the mass will move outward and continue to do so, since having left the mass they are no longer impeded by collisions This escape represents the well known tendency of unconfined gases to expand indefinitely On the other hand, if the gas is enclosed in a vessel certain molecules which possess outward directed velocities impinge upon the walls of the vessel The normal components of the momenta of these molecules are reversed by the impact so that a pressure is exerted on the walls This is the ordinary gas pressure

The molecules of a gas exert in general an attractive force on one another which is very small unless the molecules are very close together When a gas is cooled or very strongly compressed a point is reached when the molecules cluster together in virtue of this attractive force and the gas is said to liquefy In the liquid state the molecular movement persists, but, the molecules being much closer together, the average distance traversed by a molecule before a collision takes place with another molecule, i e the mean free path, is very much smaller

The attractive forces between the molecules in the liquid state are no longer small as in the gas, and, moreover, they must differ in different directions round the molecule since all molecules possess a more or less complicated structure When the liquid is cooled a point is reached where the molecules orientate themselves in such a way as to place their regions of maximum attraction as close together as possible and a solid of definite structure is produced The molecules of the solid are still capable of vibratory motion, but progressive translatory motion of the molecules no longer takes place.

The dynamical theory of heat states that the heat content of a body is simply the energy of molecular agitation, together with the potential energy of separation of molecules which exert attractive forces on one another. The reasons for believing heat to be a form of energy, or in Tyndall's original phrase 'a mode of motion,' are well known Consider the conditions of Joule's experiment on the Mechanical Equivalent of Heat A falling weight would if free acquire kinetic energy In Joule's experiment, however, it is prevented from getting up speed and made to churn up water with a paddle-wheel The motion which the weight would have acquired is given to the water. It does not persist, however, in the form of visible motion of the mass of water, but is communicated to smaller and smaller parts of the mass, which churn through one another in random directions Finally all visible motion of the water disappears, and passes all into the separate molecules Their motion is completely chaotic, as many are moving in one direction as in another, so that the mass as a whole has no resultant motion Mass motion has passed into molecular motion and the water is found to have become hotter.

It is not therefore surprising that heat changes accompany most physico-chemical processes, since these are concerned with changes in molecular constitution and aggregation

We find that vaporisation of a liquid takes place with absorption of heat Vaporisation involves separation of the molecules against the attractive forces, and thus the performance of work The velocities of two molecules which are moving away from each other against the attractive forces will be diminished Their potential energy increases while their kinetic energy decreases. After vaporisation has taken place the molecules on the average will be moving more slowly and the temperature will have fallen unless the process takes place sufficiently slowly for heat to be absorbed from the surroundings and maintain the temperature constant

Analogous considerations apply to the intramolecular re-arrangements constituting chemical change

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is simply a special case of the general law of the conservation of energy We know that the energy content of an isolated mechanical system is constant, though its form may change The energy of a pendulum bob, for example, is wholly kinetic at the instant when it passes through the equilibrium position, and wholly potential at the end of a swing, and the kinetic energy which it possesses in the one case is equal to the potential energy which it possesses in the other

Now let us consider what happens when two equal, completely inelastic masses moving with equal and opposite velocities impinge directly Both are brought to rest, their kinetic energy disappears and the masses get hot This means that their molecules have gained kinetic energy, and since the masses have probably expanded owing to the rise in temperature the molecules have gained potential energy as well It is clear mechanically that the loss of kinetic energy of the two masses must be equal to the sum of all the kinetic energies and the potential energy gained by the individual molecules, so that the amount of heat produced will be quantitatively equivalent to the amount of mechanical energy which has disappeared

The matter would be exceedingly simple if we had direct cognisance of the molecular velocities and knew all about the molecular attractions, but, since direct knowledge on these points is not available, we are obliged to make use of an empirically determined quantity, the Mechanical Equivalent of Heat This is the ratio of the mechanical energy, measured in the appropriate mechanical units, which disappears to the amount of heat produced, measured in the conventional heat units, e g in calories, a calorie being the quantity of heat required to raise the temperature of a gram of water from 15° to 16° C The experimental determination of this ratio is described in all elementary text-books of physics One calorie is equivalent to $4\ 184 \times 10^7$ ergs

HEAT AND TEMPERATURE

We have seen that in terms of the dynamical theory the heat added to a body is the increase in kinetic and potential energies of the molecules Heat may be added to a body with or without causing its temperature to rise When latent heat of vaporisation is absorbed, it is employed in overcoming molecular attractions, and therefore increasing the potential energy of the molecules without necessarily influencing their kinetic energy The temperature of the system does not change although heat is absorbed Similarly, when latent heat of fusion is absorbed the molecules of a solid body cease to be definitely orientated with respect to one another, that is to say, their points of maximum attraction are no longer at the minimum distance from one another, and there is thus an increase in potential energy The latent heat absorbed is mainly utilised in bringing about this increase of potential energy due to de-orientation, although there may be a further change in potential energy due to actual change in the distance apart of the molecules, which will be positive or negative according as there is an increase or a decrease in volume on fusion The main point is, however, that there is not necessarily a change in kinetic energy. Fusion and vaporisation are necessarily associated with changes in the potential energy of the molecules, therefore, but not with changes in kinetic energy, moreover, both may occur at constant temperature It appears plausible, therefore, to suppose that while heat comprises the total energy, temperature is in some way only dependent upon the kinetic energy of the molecules We shall see that this supposition is correct.

The idea of temperature now requires a little more discussion. We have so far used the term without definition because everybody has a working knowledge of what temperature means, and formal definitions tend sometimes to obscure rather than clarify

Scales of temperature have been devised to give precision and reproducibility to the primarily sensational qualities of hotness and coldness We know for example that a gram of mercury when surrounded by melting ice occupies a smaller volume than when surrounded by boiling water We are also aware that ice is 'cold' while boiling water is 'hot,' and agreeing to take the temperature of melting ice and that of boiling water as fixed points on a scale, i e 0° and 100° C, we decide that the temperature of bodies of intermediate 'hotness' shall be measured by the volume which the mercury assumes when placed in contact with them This is of course in principle a perfectly arbitrary scale, but since several arbitrary scales established in this way lead to approximately concordant results for temperature measurements, one is justified in placing some degree of confidence in them

One of the most satisfactory of the practical scales, namely, the perfect gas thermometer scale, turns out also to be very interesting theoretically because it leads us to a simple physical interpretation of temperature In the constant volume gas thermometer increase of temperature is measured by the increase of pressure of a constant volume of a gas which obeys Boyle's Law as closely as possible We find that gas thermometers of the same volume which are filled to the same pressure with different gases at the temperature of melting ice will also register the same increased pressures when immersed simultaneously in a bath of hot liquid (provided small corrections be made for the deviations of the gases from Boyle's Law), so that the gas scale is independent of the nature of the gas

The idea which we are most readily able to grasp is that of equality of temperature of two bodies We will therefore proceed by endeavouring to ascertain what physical condition determines equality of temperature. When bodies have the same temperature there is no flow of heat from one to the other if they are placed in contact. Two gas thermometers adjusted at the temperature of melting ice to give the same reading have always the same temperature when they indicate the same pressure In other words, the temperature of a gas which obeys Boyle's Law is proportional to its pressure. We must therefore find out what property of the molecules of a gas it is which increases in direct proportion to the pressure

The pressure exerted by a gas according to the kinetic theory is due to the bombardment of the walls of the containing vessel, and is numerically equal to the change of molecular momentum per unit area in one second.

If n is the number of molecules contained in one cubic centimetre, m, the mass of a single molecule, and $\bar{u}^2$ the average value of the square of the velocity of the individual molecules Then it is easily shown that p, the pressure, is given by the equation

$$p=\tfrac{1}{3}nm\bar{u}^2.$$

If now equal volumes of two gases exert the same pressure we have $p=\frac{1}{3}n_1m_1\bar{u}^2=\frac{1}{3}n_2m_2\bar{u}_2^2$, and in accordance with the gas scale we say they have the same temperature

Let us now *assume* Avogadro's hypothesis, as we are justified in doing on chemical grounds This states that at the same temperature and pressure equal volumes of gases contain equal numbers of molecules, i e $n_1=n_2$, so that $m_1\bar{u}_1^2=m_2\bar{u}_2^2$, or $\frac{1}{2}m_1\bar{u}_1^2=\frac{1}{2}m_2\bar{u}_2^2$ The mean kinetic energies of molecules of different gases at the same temperature are equal, and this is the condition that there shall be no flow of heat from one to the other

For the sake of simplicity we have assumed Avogadro's hypothesis on no grounds other than purely chemical ones, but this assumption would not have been necessary if we had been prepared to make a rigorous analysis

It may indeed be shown on the principles of the kinetic theory that the condition that there should be no transfer of molecular energy from one gas to another is that the average kinetic energies of the molecules of the two gases should be equal It should be realised that this is not self-evident without the introduction of Avogadro's hypothesis Still less evident is the general proposition regarding the condition that there shall be no transfer of molecular energy between two bodies which are not perfect gases Before discussing this we must briefly consider the various types of molecular energy which make up the total heat content or internal energy of a body

In the first place we have the broad division into kinetic energy and potential energy The kinetic energy is partly due to the translational motion of the molecules, partly due to their rotational motion, and partly to the relative motion of the separate parts of the molecules as they vibrate The potential energy is partly due to the separation of molecules against attractive forces, and partly to their displacement from the most stable orientation with their points of maximum attraction as close together as possible, the intramolecular vibrations are likewise associated with potential energy Each type of kinetic energy may be resolved into three components at right angles to one another, for the velocity which determines the translational kinetic energy may be resolved into three rectangular components, while rotational kinetic energy may be split up into components about three mutually perpendicular axes of rotation Similarly, each potential energy term may be resolved into three components.

Each component of each type of possible motion represents what is called a *degree of freedom* It is clear that the total energy content of a body may be made up in a number of different ways according to the types of molecular movement which take place, e g a monatomic gas possesses only kinetic energy of translation The specific types of molecular motion and of molecular potential energy found in different substances in their various states of aggregation are not of immediate importance

What we are now concerned with is the condition for thermal equilibrium between two bodies in contact, or in other words, the criterion of temperature equality The two bodies, each of which may possess all or any of the types of molecular energy which have just been enumerated, are to be imagined in contact with one another in such a way that energy could be transferred from one to the other by collisions between molecules of the one and molecules of the other This could happen easily if one body were a solid, and the other a gas placed in contact with it If both substances are in the gaseous state they may be actually mixed, but this is in no way necessary They can be separated by a conducting wall to which they can impart energy or from which they can draw it, until their temperatures are equalised

When a single collision occurs every component of the energy of each molecule, translational, rotational, vibratory and potential, is altered in a way which could be calculated if the exact conditions of impact were known These are not known in the case of any given molecule, but by adopting the statistical method, and averaging the results of every possible type of collision it may be shown that there will be no net transfer of energy from one body to the other if, on the average, each component of each type of *kinetic* energy is equal for the two bodies Thus, for example, if we resolve the translatory motions of the molecules of each system along three axes, x, y, and z, then the average kinetic energy of all the molecules of the first body due to their motion along the x axis will be equal to the average kinetic energy of all the molecules of the second body referred to the x axis The same thing applies to the y and z axes, and analogous conditions hold in respect of the various components of rotational and vibrational kinetic energy This is the condition for equality of temperature The kinetic energy is the factor which determines temperature, heat which is utilised in increasing potential energy is usually of the nature of latent heat

The mechanical principle of equipartition of kinetic energy among the various degrees of freedom is thus the basis for the physical interpretation of temperature It is a perfectly general dynamical result, but true only on the average for large numbers of molecules Indeed, temperature itself has no meaning except in its application to a system consisting of many molecules A single molecule has no temperature The molecules of a gas may have almost any speeds from zero up to extremely high values If we wished to call those molecules with much kinetic energy 'hot' molecules and those with little 'cold' molecules, then at every temperature a gas would have to be regarded as a mixture of 'hot' and 'cold' molecules But the temperature of the gas depends upon the average value around which the individual kinetic energies are grouped, and it is this average which determines the flow of molecular energy to or from the system

We will endeavour to make the matter finally clear by considering two specific cases in which the intimate nature of the molecular motions is known We take, for example, a gram molecule of argon, and a gram molecule of oxygen The molecules of argon execute no motions save translatory ones Thus, if m be the mass of a single molecule, n the number of molecules per c c, V the volume occupied by the gram molecule, and $\bar{u}^2$ the average value of the square of the velocity, then the total energy contained in the gram molecule of argon is $\frac{1}{2}m\bar{u}^2 \times nV$

But the pressure is given by the relation

$$p = \tfrac{1}{3}nm\bar{u}^2,$$

$$pV = \tfrac{1}{3}nm\bar{u}^2 \times V,$$

but $pV = RT$ by the gas laws,

where T is the temperature given by the gas scale

Therefore $\frac{1}{3}m\bar{u}^2 \times nV = RT,$

whence $\frac{1}{2}m\bar{u}^2 \times nV = \frac{3}{2}RT$

The total energy contained by a gram molecule of argon is thus $\frac{3}{2}RT$ But the velocity of a molecule may be resolved along three axes, there are thus three degrees of freedom. The kinetic energy per degree of freedom is $\frac{1}{2}RT$

By the equipartition principle this must be true of any mechanical system each degree of freedom contributes $\frac{1}{2}RT$ to the total energy, in the form of kinetic energy

The oxygen molecule is capable not only of translational motion but of rotational motion, which introduces two more degrees of freedom If the x axis be taken as that joining the two atoms of the molecule, then it is capable of rotating about the y and z axes About the x axis it behaves dynamically as a point, being 'monatomic' about the line joining its two constituent atoms The five degrees of freedom each contribute $\frac{1}{2}RT$ to the total energy of the gram molecule of oxygen, which thus amounts to $\frac{5}{2}RT$

The criterion of temperature equality given by the equipartition principle is that the kinetic energy per degree of freedom shall be equal for the two gases There is then no net transfer of energy from one to the other on mixing But since the molecules of oxygen possess five degrees of freedom whilst the molecules of argon possess three only, the total energy of the gram molecule of oxygen is greater than that of the argon in the ratio of five to three For equal temperatures, therefore, oxygen contains more heat than an equimolecular quantity of argon

It will be observed that the temperature T measured on the gas scale corresponds with the dynamical requirements exactly

It is proportional to the pressure of the gas The pressure is proportional to $\bar{u}^2$, and therefore to the total translational energy of the molecules Translational energy corresponds always to the same number, viz three degrees of freedom; the pressure is therefore proportional to the energy per degree of freedom, whether or not rotations and vibrations are also executed by the molecules

The temperature of a solid or a liquid is best defined in terms of the temperature of the perfect gas—or real gas, corrected for deviations from Boyle's law—with which it is in thermal equilibrium, neither imparting energy to the gas nor receiving energy from the gas as a result of impacts of the gas molecules on the boundary surface

Apart from a certain practical advantage, this method of defining the temperature of solids and liquids avoids difficulties due to certain limitations which the quantum theory places upon the application of the equipartition principle to motions other than translational

TOTAL INTERNAL ENERGY

It is clear that unless the molecular mechanics of a body are accurately known it will be impossible to ascertain the exact fate of any heat it may absorb From the thermodynamical standpoint, therefore, the more general conception of total internal energy is made to suffice If a gram of a substance of constant specific heat σ is heated through θ° at constant volume, it absorbs $\theta\sigma$ calories of heat, and its total internal energy is said to increase by that amount If the specific heat is variable the internal energy increase is $\int\sigma d\theta$ Change of state may intervene in which case the internal latent heat of the change must be added to the specific heat terms Thus, if one gram of a substance of which the internal latent heat of fusion is λ calories per gram, be heated at constant volume from a temperature θ_1 below the melting point, T, to a temperature θ_2 above the melting point the change in total internal energy is

$$\int_{\theta_1}^{T}\sigma_1 d\theta+\lambda+\int_{T}^{\theta_2}\sigma_2 d\theta$$

where σ_1 is the specific heat of the solid and σ_2 that of the liquid

These changes have been assumed to take place at constant volume If the volume of the system changes a new factor intervenes, namely, the *external work performed by the system* As an example, we may take the most familiar case of a body acted upon simply by the pressure of the atmosphere If such a body expands it overcomes through a certain distance the weight of the atmosphere and thus does work If, therefore, heat is communicated to it while its volume is allowed to increase the whole of the heat will not contribute to the increase in internal energy, but part will be employed in providing the energy required to overcome the external pressure

As a general statement we have therefore

Heat supplied $(Q)=$ *Increase of total internal energy* $+$ *external work performed* (1)

This is regarding the matter from the point of view of the fate of heat supplied to the body An equivalent way of regarding the thing is to consider in what ways a decrease in the internal energy of the body may manifest itself. The body may simply yield up heat to the surroundings, in which event we should have to say that the decrease in internal energy was equal to the heat given out On the other hand, all the heat may not be yielded up to the surroundings, some may be utilised again in doing external work, as when a gas expands against external pressure, and in this case we should have the statement, which is of course exactly equivalent to the original statement.

Decrease in internal energy=Heat yielded up + external work performed (2)

Certain symbols are conventionally used, namely,

U=decrease in total internal energy
Q=heat absorbed by (supplied to) the system
A=external work performed by the system

Statement (1) thus becomes $Q=(-U)+A$, while statement (2) becomes $U=-Q+A$, or in each case,

$$Q=A-U$$

This is the form in which the first law of thermodynamics is frequently applied

THE SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics emphasises the fundamental similarity of heat changes and other energy changes It is the direct expression of the mechanical theory of heat The second law deals with a peculiar limitation to which heat changes are subject This may be illustrated by considering further the case of the two equal inelastic masses, the kinetic energy of which was completely converted into heat after collision The mass motion was completely converted into random molecular motions, no energy being lost No energy would be lost if the process were reversed, and the heat motion of the molecules were reconverted into motion of the masses as a whole But this involves the unfamiliar event of a mass suddenly cooling itself and starting from rest without the application of external force; moreover, looked at purely from the standpoint of the kinetic theory it is an improbable occurrence for the following reasons.

In each of the moving masses before impact the total energy is made up of two parts, one dependent on the internal movements of the molecules, the other on the bodily movement of the mass The bodily movement of the mass simply means that every single molecule has superimposed on its thermal movement an additional directed component equal to the velocity of the mass The thermal movement is completely random, as many molecules on the average have velocities directed in one direction as in the opposite direction, so that no visible displacement of the body results, but the common directed component manifests itself as the motion of the whole body through space

Then the collision between the two masses takes place.

If the masses were elastic the directed components of the molecular velocities at the point of impact would simply be reversed, and this reversal would be transmitted by molecular collisions throughout the masses, so that they would move off from one another with their original velocities reversed, but the collision being inelastic, the recoil of the molecules at the point of impact takes place in all directions, and as the result of the subsequent molecular collisions throughout the whole body the original directed velocity components of the molecules are now distributed in all directions The directed components of the molecular velocities become inextricably mixed up That is to say, the mass kinetic energy is converted into heat

Now, clearly, it is one thing to mix up a number of directed components and quite another thing to sort them out again, just as a pack of cards, arranged in suits and sequences, may easily be mixed by shuffling, although no amount of reshuffling is likely to sort the cards out again

This is why a body cannot do work merely by cooling itself and remaining otherwise unchanged. The second law of thermodynamics rests upon this foundation In one of its several forms it states *that it is impossible to derive a continuous supply of work by utilising the heat of bodies at uniform temperature, these bodies remaining otherwise unchanged*

The preceding argument might seem at first to imply that heat cannot be converted into work at all Reflection shows that this is not a just implication If we have a gas confined in a non-conducting cylinder by a piston, and if the pressure of the gas is greater than the external pressure, then those molecules of the gas which happen to be moving in the right direction may communicate some of their kinetic energy to the piston and enable it to move outward against the external pressure, thereby doing work The gas molecules having lost kinetic energy, the gas is cooled Work has therefore been done at the expense of the heat of the gas But the essential point to notice is that the gas is changed not only in respect of having lost heat, but also in that it now occupies a larger volume The case is fundamentally different from that of a gas, some of whose molecular kinetic energy is converted into mass kinetic energy of the whole gas, the volume remaining unchanged Heat has been converted into work, *but something else has happened as well* This is what we always find there are many different devices for the conversion of heat into work, but, whatever the nature of the device may be, we always find, as a consequence of the nature of heat, that something besides the conversion must happen simultaneously, or, in thermodynamical language, there must be '*compensation*' In the example just given this compensation consisted in the change of volume of a gas, i e the movement of the molecules further apart

When heat is transformed into work we have the equivalent of an 'unmixing' of the molecular velocities, since the work gained might appear in the form of a directed kinetic energy of the whole mass of a substance This by itself constitutes a change not in accordance with the principles of probability, but the 'compensation' is usually found to consist in an increase in the probability of the actual arrangement of the molecules in space The arrangement of a given number of molecules in a large volume is a more probable state than their arrangement in a small volume This may easily be realised by reflecting that the spontaneous contraction of all the molecules of a gas into, say, one-half of the containing vessel would require a combination of hazards in the molecular motion which would be exceedingly unlikely to occur Hence, the increase in the probability of the arrangement of the molecules in space when a gas expands compensates for the 'unmixing' of the molecular velocities which accompanies the transformation of heat into work, and which is an 'improbable' happening

When we come to consider Carnot's cycle in Chapter III we shall find that by an ingenious series of changes we can bring the gas back to its initial volume, and yet gain work from heat But in this case we shall see that the 'compensation' consists in the simultaneous passage of a certain quantity of heat from a heat reservoir at a higher temperature to one at a lower temperature.

By considering the irreversibility of the conversion of mass energy into molecular energy, which results from the extreme improbability of the random molecular motions all simultaneously acquiring a common directed component, we arrived at a statement of the second law of thermodynamics

Exactly the same principle leads to a useful alternative statement of the second law, which is as follows *Heat cannot spontaneously pass from a colder to a warmer body* For consider two bodies A and B, the temperature of A being higher than that of B The velocities of the molecules of *A* are greater than those of the molecules of *B*. If the bodies are placed in thermal contact their temperatures gradually become equal. The molecular velocities are now no longer divided into two groups; they have become 'mixed.' Velocities are, in a sense, things just as definite as grains of sand, and, just as it is highly improbable that a bushel of red sand and a bushel of white sand once mixed will ever become separated again by stirring, so it is equally improbable that the molecular velocities will ever divide themselves spontaneously into two groups again. The temperatures having become equalised will remain equal. The passage of heat from a colder to a hotter body means that the cold body would get still colder and the hot body still hotter, which is exactly the same thing as the reversal of a previous partial equalisation of temperature. The Second Law states that this does not occur, and is thus simply asserting a necessary consequence of the molecular nature of matter and the kinetic nature of heat.

LIMITATIONS OF THE SECOND LAW

It will be seen that the second law of thermodynamics is not absolute. There is nothing mechanically impossible in the sort of process which it rules out. The direction of motion of individual molecules changes continually in a way which, regarding large numbers of them together, we can only describe as random. It may so happen that at one instant all the molecules of a body chance to be moving in the same direction—or, what is quite sufficient, to have a common component in one direction. The body then moves off as a whole. Indeed, it is probable that if we only wait long enough something of the sort will happen. The waters of the Red Sea could have divided from natural causes; the Pyramids might have reared themselves or the Andes might have risen from the plains at the expense of molecular energy. But the extreme improbability of any of these occurrences is realised when the number of molecules in a gram molecule is known to be $6{\cdot}1 \times 10^{23}$. If we reflect on the number of unsuccessful trials which would accompany one successful attempt to sort by shuffling the fifty-two cards of a pack, no surprise is felt that the second law of thermodynamics is true in practice. Calculation shows that a lead weight is not likely once in geological ages to rise a millimetre from the ground

But the validity of the second law depends entirely upon the smallness of molecules, and the vastness of the numbers contained in all ordinary bodies For systems composed of limited numbers of molecules, such as small colloidal particles, the deviations from the law cease to be inappreciable The Brownian motion is a manifestation of the transformation of molecular motion into the mass motion of a particle, and a violation of the second law The smaller the particle the greater the motion There is no sharp line between small colloidal particles and complex molecules The Brownian movement is at the same time mass motion and molecular motion

CHAPTER II

APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

THE WORK DONE BY THE EXPANSION OF GASES

IN thermodynamical reasoning we have frequently to deal with the expansion of gases, and to calculate the work performed during the expansion

Let us therefore consider a gas confined in a cylinder fitted with a frictionless weightless piston We can imagine that the natural tendency of the gas to expand and push the piston out is just counterbalanced by a weight placed on the piston

Let the area of the piston be A, and let the pressure of the gas be p_1

Pressure = Force per unit area, therefore the total force exerted by the gas on the piston is p_1A, and this is equal to the weight w_1 which keeps the piston in equilibrium Let the volume now occupied by the gas be v_1 Suppose this weight be replaced by a smaller weight w_2, then the piston will move upwards and the volume of the gas will increase until its pressure falls to a new value p_2 such that $p_2A=w_2$

If the temperature remains constant and the gas obeys Boyle's law, we shall have $p_1v_1=p_2v_2$, where v_2 is the new volume occupied by the gas

The actual state of affairs at any moment during the progress of the expansion depends upon the suddenness with which the weight is changed If a sudden diminution of the weight occurred the piston would fly upward with some speed, the actual speed being greater and greater the more the piston approximated to the ideal condition of masslessness

It happens not to be particularly fruitful to consider catastrophic changes of this nature, it is more profitable to think of the change occurring in a certain well-ordered manner which is known as *reversible* At a later stage we shall have to discuss reversible processes in some detail, we may, therefore, describe how the expansion of the gas in the cylinder from volume v_1 to volume v_2 may be allowed to take place reversibly

Imagine the weight w_1 to diminish by an infinitesimal amount δw, then the volume of the gas will increase by an amount δv, and the pressure will fall, in accordance with Boyle's law, to a value $p_1 - \delta p$, provided that the temperature remains constant Here $A\,\delta p = \delta w$ Now imagine the weight to decrease continuously and very slowly, so that at every instant the piston has moved into such a position that the pressure of the gas has adjusted itself to the exact value which Boyle's law gives for the equilibrium pressure corresponding to the actual volume of the gas At every instant of time the pressure of the gas is exactly balanced by the weight, except that there is just an infinitesimal excess of pressure over the amount required to support the weight The system is never removed by more than an infinitesimal amount from equilibrium, and if the pressure at any moment is plotted against the volume the values will lie on the curve given by Boyle's law Under these conditions the change is said to take place reversibly because by an infinitesimal increase in the weight at any instant the movement of the piston would be reversed

In general, any change is said to take place reversibly when the driving force exceeds the opposing force by an infinitesimally small amount A reversible change is the nearest possible approach to the limiting case where driving and opposing forces are equal, that is, to a state of equilibrium Duhem (Mécanique Chimique) describes a reversible change in these words, "Une modification réversible est une suite continue d'états d'équilibre, limite commune de deux groupes de modifications réalisables de sens inverse"

The reversible isothermal expansion of a gas is an important case because the relation between pressure and volume at every point of the operation is known to be that given by Boyle's law During the sudden expansion ensuing upon a finite reduction of pressure the relation between pressure and volume at any instant is quite arbitrary, in this case the work done during the expansion cannot be calculated, because, as we are about to see, this calculation depends upon a knowledge of the equation connecting p and v

CALCULATION OF THE WORK PERFORMED IN THE ISOTHERMAL REVERSIBLE EXPANSION OF A PERFECT GAS

Let the pressure be p, the volume v, and the area of the piston A

Total force on piston $=pA$

If the piston moves outward through a distance dx, the work done $=$ force $\times$ distance $=pA\,dx$.

$$A\,dx = \text{change in volume} = dv$$

$$\text{Work done} = dW = p\,dv$$

For expansion between the finite limits v_1 and v_2 we have

$$W = \int_{v_1}^{v_2} p\,dv$$

To integrate this we must know the relation between p and v.

Since the change is reversible the pressure and volume at every point are the equilibrium values, that is, they are given by Boyle's law

$$pv = k\theta,$$

$$W = \int_{v_1}^{v_2} \frac{k\theta\,dv}{v},$$

$$= k\theta\,ln\frac{v_2}{v_1} = k\theta\,ln\frac{p_1}{p_2},$$

since θ is constant

ln stands for the logarithm to the base *e*

The actual value of k depends of course on the quantity of gas taken Since one gram molecule of all gases under the same conditions of temperature and pressure occupies the same volume, k will be the same for all gases if we consider in each case a gram molecule of the gas In this case the conventional letter to use is R.

We have thus, that when a gram molecule of any gas expands from volume v_1 to v_2 the work performed is

$$R\theta\,ln\frac{v_2}{v_1}$$

For n gram molecules the quantity is $n\,R\theta\,ln\frac{v_2}{v_1}$

The numerical value of R may be calculated as follows

1 gram molecule of any gas which obeys the laws of ideal

gases occupies a volume of 22 4 litres at 0° C and a pressure of 760 mms of mercury

0° C on the absolute scale = 273 1°

A pressure of 760 mms of mercury = weight of a column 76 cms in height exerted on an area of 1 square centimetre

$=76\times 13\ 59$ grams weight per square cm

$=76\times 13\ 59\times 981$ dynes per square cm

Thus $p=76\times 13\ 59\times 981$ dynes per square cm ,

$v=22{,}400$ c cs ,

$\theta=273\ 1$,

whence $$R=\frac{pv}{\theta}=\frac{76\times 13\ 59\times 981\times 22{,}400}{273\ 1}\text{ ergs per degree,}$$

$$=\frac{76\times 13\ 59\times 981\times 22{,}400}{273\ 1\times 4\ 184\times 10^7}\text{ calories per degree,}$$

$$=1\ 98\text{ calories per degree}$$

The mechanical work performed when a gas expands against an opposing pressure might be derived from one or both of two sources—the internal energy of the gas, and the heat which it absorbs from its surroundings during the process of expansion But it has been shown by Joule that the internal energy of a perfect gas is independent of the volume it occupies and, therefore, of the pressure. This was proved by allowing a gas to expand from a vessel at known pressure into a vacuum No work is performed in this process since there is no opposing force to be overcome, but the volume of the gas increases and its pressure diminishes If the internal energy changed there would have to be an absorption or evolution of heat, since, there being no external work, any change in the internal energy of the gas could only manifest itself in the form of heat But actually no heat is absorbed or given out, and no temperature change is observed when the expansion into a vacuum takes place in well-insulated vessels. The Joule experiment thus leads to the conclusion that the internal energy of a perfect gas is independent of the volume

This result is to be expected according to the kinetic theory, for in a gas which satisfies Boyle's law the attractive or repulsive forces between the molecules are small enough to be neglected, and therefore no work is done against internal attractive forces—or by internal repulsive forces—when the gas passes into a greater volume When, therefore, expansion takes place against external pressure, the work performed must be derived from the heat of the surroundings This heat is absorbed continuously by the gas during the process of expansion If the gas were insulated from the surroundings the expansion could not take place isothermally at all and the gas would cool During an '*adiabatic*' expansion against an opposing pressure, that is an expansion during which the gas is thermally insulated, cooling actually takes place

During the expansion of a perfect gas from volume v_1 to volume v_2, at constant temperature, we have, then, that the mechanical work performed is $k\theta \, ln \frac{v_2}{v_1}$ when the process takes place reversibly, and that this work is equivalent to the heat absorbed from the surroundings If the surroundings cannot supply the heat at the necessary rate, then it simply means that the expansion cannot take place isothermally It may be instructive to describe the process in terms of the kinetic theory, because thermodynamic processes tend to appear unreal and purely formal unless constantly regarded from this standpoint Certain of the gas molecules collide with the piston, yielding up some of their kinetic energy and pushing it outward against the opposing force As a result the mean kinetic energy of the molecules tends to decrease and the temperature to fall If no heat is supplied from without the temperature falls continually as more and more of the kinetic energy of the molecules is yielded up in collisions with the piston This corresponds to the adiabatic expansion If the walls of the containing vessel are conducting and are maintained at constant temperature, i e if the average kinetic energy of their molecules is maintained at a certain level, the gas molecules regain their lost kinetic energy by collision with the walls This is the isothermal process, where the energy needed to force back the piston is ultimately derived from the surroundings

THE SPECIFIC HEATS OF GASES

So far the processes considered have concerned expansion against a regulated external pressure, and the heat absorption has merely kept pace with the requirements of the system for the maintenance of constant temperature We will now consider what happens when a given quantity of heat is put into a gas, and other things are left to adjust themselves accordingly

Two important cases arise

(i) The volume of the gas is maintained constant. In this case there can be no external work performed, and the heat is simply utilised in raising the temperature of the gas. The quantity of heat required to raise the temperature of a gram molecule of gas $d\theta°$ at constant volume is $C_v d\theta$ where C_v is the '*Specific heat at constant volume*.' It represents the increase per degree of the internal energy of the gas.

(ii) The gas is allowed to expand against a uniform external pressure. Heat will in this case be utilised in performing external work, so that to raise the temperature of one gram molecule of the gas $d\theta$ degrees a larger amount of heat than before is required, $C_p d\theta$, where C_p is the *specific heat at constant pressure*.

The difference between C_p and C_v may be measured experimentally. The value will be expressed in thermal units. The mechanical work upon the performance of which this difference depends may readily be calculated in mechanical units. By comparing the two values the mechanical equivalent of heat may be found. This calculation was performed by Julius Meyer, and was the first determination of the mechanical equivalent.

When a quantity of heat C_p is given to the gas at constant pressure let the volume increase by an amount dv. The external mechanical work is pdv. This is not performed when the heat is added at constant volume. Therefore

$$C_p d\theta = C_v d\theta + pdv$$

But

$$pv = R\theta,$$

or, since p is constant $pdv = Rd\theta$ in mechanical unit $= \frac{Rd\theta}{J}$ in thermal units

Therefore

$$C_p d\theta = C_v d\theta + \frac{Rd\theta}{J},$$

$$C_p - C_v = \frac{R}{J}$$

For all gases which behave in approximate accordance with Boyle's law the difference between the two specific heats is found to be 1.98 calories.

R is known in mechanical units, whence J may be calculated.

The best value of J from direct experiment is $4{\cdot}184 \times 10^7$

ergs per calorie, so that by a converse method of calculation $C_p - C_v$ may be found

In order to simplify equations it is customary to omit the factor J, and to take it for granted that all the quantities are expressed in the same units, either all in mechanical units or all in thermal units

THE EQUATION OF AN ADIABATIC TRANSFORMATION OF A PERFECT GAS

It is required to find the relation between the pressure and volume of a perfect gas, to which no heat is added and from which no heat is removed

We consider the fate of a quantity dQ of heat added to the gas Some of it may go to raise the temperature, or in other words, to increase the internal energy of the gas, the rest is utilised in the performance of work by expansion against the external pressure Expressing this by an equation we obtain

$$dQ = C_v d\theta + p dv \qquad (\text{i})$$

which is a perfectly general relation

For an adiabatic transformation $dQ = 0$, and thus

$$C_v d\theta + p dv = 0 \qquad (\text{ii})$$

Any external work is performed at the expense of the internal energy of the gas itself

Equation (i) regards the total change as made up of two parts, which, when both are infinitesimally small, may be regarded as independent These are, namely, one in which the internal energy increases by $C_v d\theta$, the volume remaining constant, and one in which expansion takes place at constant temperature with performance of work pdv

We are seeking a relation between p and v Therefore, $d\theta$ must be eliminated All possible values of p, v, and θ are connected by the relation

$$pv = R\theta$$

Differentiating this

$$pdv + vdp = Rd\theta,$$

therefore

$$d\theta = \frac{pdv + vdp}{R}$$

We replace $d\theta$ by this value and obtain from (ii)

$$\frac{C_v(pdv + vdp)}{R} + pdv = 0$$

We have already proved that

$$C_p - C_v = R,$$

therefore
$$C_v(pdv + vdp) + (C_p - C_v)pdv = 0,$$
$$C_p pdv + C_v vdp = 0$$
$$\frac{C_p}{C_v}\frac{dv}{v} + \frac{dp}{p} = 0,$$

Integrating $C_p/C_v \; ln\, v + ln\, p = \text{constant}$

C_p/C_v is usually denoted by γ

Thus, $\gamma\, ln\, v + ln\, p = \text{constant},$

or $pv^\gamma = \text{constant}$

HEAT OF REACTION AND ITS VARIATION WITH TEMPERATURE

The term heat of reaction is here taken in the most general sense, and includes the different kinds of latent heat, such as latent heat of fusion, vaporisation, and allotropic change, as well as the heat changes which accompany purely chemical reactions

It will be well first to clear out of the way an extraneous factor which complicates all considerations of heat of reaction. If a system suffers a transformation accompanied by an increase of volume, work is done in overcoming the external pressure A claim is thus made on the thermal resources of the system, which diminishes a positive heat of reaction, and makes a negative heat of reaction still more negative When the reaction is accompanied by a decrease in volume, the converse holds good It is inexpedient always to introduce this factor into equations because it complicates them unnecessarily, but it must always be remembered and allowed for For example, the reaction $2H_2 + O_2 = 2H_2O$ is accompanied by the evolution of a large quantity of heat, and the volume decreases by V litres for every two gram molecules of steam formed, if the pressure remains constant V is the volume occupied by a gram molecule of any gas The work done on the system by the atmospheric pressure—assuming that to be the constant external pressure—is

$$\int pdv = p\int dv = pV = R\theta$$

Expressed in thermal units this is approximately 20 calories. The heat evolved in the reaction is therefore greater by this amount than it would have been if the reaction took place at constant volume.

In general, to find the heat of reaction at constant pressure, it is necessary to add $R\theta$ calories to the heat of reaction at constant volume—taken as *positive* if heat is *evolved*—for every gram molecule of gas which disappears in the reaction, and to subtract $R\theta$ calories for each gram molecule which appears

In what follows, heat of reaction will be assumed to be corrected for the external work due to any volume changes accompanying the reaction

It is important to realise that if a substance A is chemically transformed into B, with the evolution of a quantity of heat U per gram molecule, then the internal energy of a gram molecule of A must exceed that of a gram molecule of B by an amount U That we are frequently—or indeed almost always—ignorant of the precise nature of the respective internal energies of A and B does not make this statement any the less definite and exact

The vapour phase of a substance changes into the liquid phase with evolution of latent heat λ per gram molecule; λ being taken as the latent heat corrected for the external work due to change in volume, that is to say, λ is the 'internal' latent heat This means that the vapour possesses an internal energy greater than that of the liquid by λ calories per gram molecule This difference, as we have already seen, represents the potential energy of separation of the molecules in the vapour phase, due to the attractive forces Monoclinic sulphur changes into rhombic sulphur with evolution of heat. Here there is a change of potential energy due to the change in the distance apart of the molecules in passing from one form to the other, and a more complicated change in potential energy due to the different orientation of the molecules in the new form There may also be changes in the number of sulphur atoms in the molecule, or unit of crystal structure, and the potential energy changes associated with this are even more difficult to predict Nevertheless, the evolution of heat which accompanies the passage from the monoclinic to the rhombic form shows that monoclinic sulphur has a higher internal energy than rhombic sulphur by an amount precisely equal to the heat of transformation (always corrected for external work)

If a gram molecule of the substance A be heated through $d\theta$ degrees its internal energy increases by $C_A d\theta$, where C_A is the molecular heat of A Similarly when a gram molecule of B is heated through the same range its internal energy increases by $C_B d\theta$ C_A and C_B in general are different Suppose C_A to be greater than C_B This means that as the temperature rises the internal energy of A increases more rapidly than that of B, or the total internal energy of A increases relatively to that of B At the higher temperature, therefore, more heat will be given out when A passes into B than at the lower temperature, or the heat of reaction increases with temperature

We have at temperature θ,

Heat of reaction $=U=$ Internal energy of A − Internal energy of B

$$=E_A-E_B$$

At temperature $\theta+d\theta$, heat of reaction $=U+dU$,

$$=E_A+C_A d\theta-(E_B+C_B d\theta)$$

$$dU=(C^A-C_B)\,d\theta,$$

or

$$\frac{dU}{d\theta}=C_A-C_B$$

If several substances react to form several others the value of $\frac{dU}{d\theta}$ becomes

Σ specific heats of reacting substances $-\,\Sigma$ specific heats of products

Thus, if the chemical change be represented by the equation,

$$n_1A_1+n_2A_2+ \qquad =n_1'B_1+n_2'B_2 \qquad +U \text{ cals}$$

$$\frac{dU}{d\theta}=n_1C_{A1}+n_2C_{A2}+ \qquad -n_1'C_{B1}-n_2'C_{B2}$$

A sum of terms such as these is usually represented simply by writing

$$\frac{dU}{d\theta}=\Sigma nC$$

THE LAW OF CONSTANT HEAT SUMMATION

This well-known chemical law now requires little discussion From what has been said it is obvious that the heat of combustion of solid sulphur to gaseous sulphur dioxide must be equal to the heat of combustion of sulphur vapour to sulphur dioxide less the heat absorbed when solid sulphur is converted into vapour Thus

$$S_{\text{solid}}=S_{\text{vapour}}-\lambda \quad \text{(absorbed)},$$

$$S_{\text{vapour}}+O_2=SO_2+U \quad \text{(evolved)}$$

Adding these two steps

$$S_{\text{solid}}+O_2=SO_2+U-\lambda$$

Expressed in words, whether we burn solid sulphur or sulphur vapour the product is the same and contains the same amount of energy The oxygen used is the same in each instance To vaporise solid sulphur heat must be supplied Sulphur vapour has therefore more internal energy than solid sulphur When it burns to the same product this excess must be liberated The heat of combustion of sulphur vapour is thus greater than that of the solid by the same amount that the internal energy of the vapour is greater than that of the solid

It is assumed that all heat terms are corrected to constant volume in the simple way explained above

CHAPTER III

THE SECOND LAW OF THERMODYNAMICS AND CARNOT'S THEOREM

CONSIDERATION of the nature of heat led us to two alternative statements of the Second Law of Thermodynamics In one form the law states that it is impossible to obtain work by abstracting the heat from a body and cooling it below the temperature of its surroundings, the body being otherwise unchanged The alternative form states that heat cannot pass spontaneously from a colder to a warmer body.

In the course of this chapter further illustrations will be given of the significance of these principles Some general remarks on the manner in which the Second Law is applied and developed are desirable at this point

Though fundamentally connected with the kinetic theory the Second Law was accepted as the result of experience, and its consequences were developed without reference to this relationship It was realised after much fruitless devising and the exercise of much unrewarded ingenuity that all processes for the utilisation of the heat of the surroundings to obtain a continuous supply of mechanical work were just as much foredoomed to failure as the cruder kind of scheme for obtaining mechanical work at the expense of nothing at all In other words, 'perpetual motion of the second kind' is just as unattainable as 'perpetual motion of the first kind' To recall an oft-quoted example, a ship cannot be propelled through the ocean at the expense of the heat of the ocean, vast as this supply may be

This principle having been accepted, a number of remarkable results may be inferred from it by purely logical processes, and without further data or assumptions For instance, from the Second Law may be found, not only qualitatively, but quantitatively the influence of temperature on the equilibrium constant of a gaseous reaction, the influence of temperature on the vapour pressure of a liquid, the relation between the freezing-point lowering of a dilute solution and the osmotic pressure, and innumerable other results All these relations might be deduced directly from the kinetic theory if we had sufficient knowledge of the molecular mechanisms involved, and in some cases can actually be derived in this way But in other cases results can be obtained from the second law concerning phenomena the mechanism of which is too obscure to admit of direct analysis Often, indeed, calculations on the basis of the kinetic theory are too difficult to carry out Having, therefore, arrived at a general principle which is confirmed by direct experience there is every reason to exploit its consequences to the utmost

Historically, this was done before the essentially kinetic basis of the Second Law was realised We shall see how the abstractly thermodynamic mode of procedure and the kinetic theory come into contact again more clearly when we consider the subject of entropy

One is struck almost immediately, however, by the fact that the Second Law seems to be a principle so general and so negative as to elude that mathematical expression which is necessary for the making of quantitative deductions The steps by which quantitative application of the Second Law is made to the problems of chemistry and physics are indeed a little recondite and indirect and require to be followed carefully

I We begin by considering a certain series of operations carried out under ideal conditions with a perfect gas, by means of which heat is converted into work The gas is made to constitute an ‘ ideal heat engine ’ and the series of operations constitutes what is known as Carnot’s cycle, after the French engineer Carnot to whom the investigation is due

A perfect gas is contained in a cylinder fitted with a frictionless piston Let pressure and volume be p_1, v_1, represented by the point A on the diagram, where pressures are plotted as ordinates, and volumes as abscissae The temperature is θ_1. The following operations are carried out

(1) The gas is allowed to expand isothermally and reversibly at θ_1 until its volume has increased to v_2 and its pressure has fallen to p_2 The new state is represented by the point B on the figure

An amount of work has been performed equal to $\int_{v_1}^{v_2} p\,dv$, this definite integral is represented by the area $APBQ$, where P and Q are the projections of A and B respectively on the v axis This work has been performed at the expense of an amount of heat Q_1, absorbed by the gas from its surroundings (or let us say for simplicity from a reservoir at temperature θ_1) It is important to realise that this is in no way contrary to the second law, which only states that work cannot be derived from the heat of a body at constant temperature *the body remaining unchanged in other respects.* In the case we are considering the heat of the gas, replenished by heat taken from the surroundings, has been converted into work, but the gas now occupies a greater volume As we have seen, this does not involve the improbable 'unmixing' of molecular velocities, which would only have to be assumed if the gas in some way performed work at the expense of its heat, and replenished this heat by absorbing more from the surroundings, its volume remaining unchanged all the while

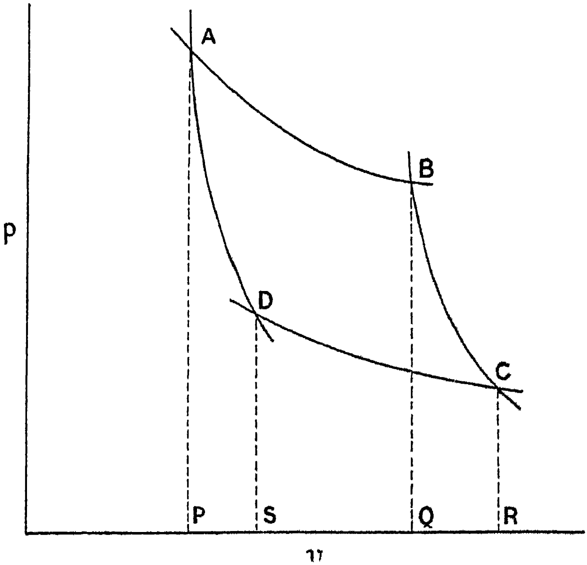

FIG 1

(ii) The gas is allowed to expand adiabatically, so that its pressure falls to p_3 and its volume increases to v_3, represented by the point C The work performed during this expansion is given by the area $BCQR$, and since the gas is insulated from its surroundings its temperature will have fallen to θ_2

Here again work has been obtained at the expense of the heat energy of the gas, but the gas itself has undergone a 'compensating' change

(iii) Let us imagine the gas now placed in thermal communication with a heat reservoir at temperature θ_2, and compressed isothermally until the point D is reached where its pressure has increased to p_4 and its volume diminished to v_4 The point D is not selected arbitrarily as B and C were, but is the point at which the adiabatic curve through A cuts the isothermal CD through C. Work has been performed on the gas during this compression, in amount equal to the area $CDSR$, and an equivalent amount of heat has been produced in the gas and yielded up to the surroundings This process, involving the conversion of work into heat, is subject to no restrictions connected with the second law

(iv) Finally, the gas is compressed adiabatically along DA until its temperature rises to the original value θ_1, and its pressure and volume return to the original values p_1 and v_1 During this process work is performed on the gas represented by the area $DSPA$

The gas has now returned in every respect to its original state, temperature, pressure and volume having assumed their initial values. The gas is said to have traversed a cycle along the path $ABCD$—the 'path' in this instance being the curve giving the relation between pressure and volume at each point of the cycle During the cycle the gas has performed work represented in amount by the sum of the areas $APQB$ and $BQRC$, and has had performed on it work represented by the sum of the areas $CRSD$ and $DSPA$ The net work performed by the gas is therefore represented by $APQB+BQRC-CRSD-DSPA=ABCD$

The work performed during the cycle is thus represented by the area enclosed by the path, which is obvious when it is remembered that the work performed is given by $\int p dv$

Work has been performed, at the expense of the heat of the surroundings since the gas has regained its original temperature, the pressure and volume of the gas are unchanged Where is the compensation which the second law asserts to be inevitable? It consists in the passage of heat from the reservoir at θ_1 to the reservoir at the lower temperature θ_2, which came about because the heat which the gas drew from the high temperature reservoir during its expansion along AB was partly returned to the low temperature reservoir during the compression CD Along BC and DA neither absorption nor rejection of heat took place Along AB an amount of heat Q_1 was absorbed from a reservoir at the temperature θ_1, and along DC an amount of heat Q_2 was rejected to a reservoir at θ_2 An amount of heat Q_1-Q_2 was converted into mechanical work during the cycle The condition of the gas at the end of the cycle was unaltered An amount of heat Q_2 passed from the reservoir at θ_1 to the reservoir at θ_2

It will be observed that for work to be performed in the cycle θ_2 must be lower than θ_1, if we tried to bring the gas back to its initial condition by compression at θ_1, so as to return Q_2 to a source at the original temperature, we should simply retrace the path BA and the net work performed in the cycle would be zero The possibility of deriving work from the cycle depends essentially on the fact that the pressure exerted by a gas is *ceteris paribus* smaller the lower the temperature (because the velocity of the molecules is less), and therefore an expansion which takes place at a higher temperature can be reversed at a lower temperature with less expenditure of work Reversal of the isothermal process at a lower temperature enables us to take the gas back to its original state without completely cancelling the work done in the first expansion, but it means of course that the heat rejected by the gas during the compression must *ipso facto* be yielded up to a body at this lower temperature

By the isothermal expansion of the gas we could obtain work at the expense of the heat reservoir, but we should have to allow the gas to change its volume. If we wish the gas itself to be unchanged, we must carry out a cycle, and, if a net supply of work is to be derived from this, passage of heat from a warmer to a colder body is inevitable.

We have just seen that this condition follows simply from the nature of a gas It ultimately depends upon the fact that gas pressure falls with temperature, and is thus an indirect consequence of the proportionality between temperature and kinetic energy

Realising that work cannot be derived from Carnot's cycle unless there is a simultaneous passage of heat from a body at a higher temperature to one at a lower temperature, we are now in a position to consider the next important step towards the application of the second law of thermodynamics This step is the introduction of a function known as the thermodynamic efficiency of a process

II In Carnot's cycle the only heat absorbed is the amount Q_1, taken in by the gas from the reservoir at θ_1

Let us regard the aim of the cycle as consisting in the transformation of the maximum possible fraction of this heat supply into work

The amount actually transformed into work was Q_1-Q_2. Q_2 had inevitably to be rejected at the lower temperature

The thermodynamic efficiency of the cycle is defined as

$$\frac{Q_1-Q_2}{Q_1}=\frac{\text{Heat transformed into work}}{\text{Heat drawn from supply}}.$$

It will be proved shortly that

$$\frac{Q_1-Q_2}{Q_1}=\frac{\theta_1-\theta_2}{\theta_1}.$$

III. Carnot's cycle is carried out with a perfect gas Similar cycles, consisting of isothermal and adiabatic expansions, can be carried out with other substances, including solids and liquids The smallness of the volume changes in the case of solids and liquids does not affect matters in principle

The isothermal expansion can be made to consist in the change of state of one of the substances, for example fusion with increase of volume In such a case Q_1 would be the latent heat

Any arrangement for carrying out such a cycle constitutes what is called a 'heat engine,' and every such heat engine could be made to operate between defined temperature limits We shall see several examples of the operation of such processes shortly The practicability of the devices used is a quite irrelevant matter

IV. We now arrive at the most important step in the argument Carnot proved that all reversible 'heat engines' have the same thermodynamic efficiency

Before giving Carnot's proof it is desirable to illustrate the importance of this theorem Let the 'heat engine' operate in the following way, having as working substance 1 gram of a solid of which the melting point is θ under a pressure p, and having a latent heat of fusion l. The first stage in the cycle is the isothermal liquefaction of 1 gram of the solid at temperature θ and under the pressure p. It is allowed to melt and absorb the requisite latent heat from the heat reservoir. The volume increases from v_1 to v_2, where v_1 is the specific volume of the solid, v_2 that of the liquid. The external work performed is $p(v_2-v_1)$, since the pressure remains constant; the amount of heat absorbed is l.

Secondly, the liquid is gradually cooled to a lower temperature $\theta-\Delta\theta$ where the solid and liquid phases are in equilibrium under a different pressure $p-\Delta p$ (melting point—i.e. temperature at which solid and liquid are in equilibrium—varies with the pressure). During this cooling the pressure is adjusted at every instant to the equilibrium value; an amount of heat $\sigma_l\Delta\theta$ is given out, where σ_l=specific heat of liquid.

Thirdly, the liquid is caused to solidify under the new equilibrium pressure $(p-\Delta p)$, by the gradual withdrawal of heat into a reservoir at $\theta-\Delta\theta$, whereby an amount of heat $l-\Delta l$ is rejected and external work $(p-\Delta p)$ (v_2-v_1) is performed on the system. In calculating the work we neglect the small variation with temperature in (v_2-v_1).

Finally, the solid is warmed up to the original melting point, the pressure is restored to the original value; $\sigma_s\Delta\theta$ is absorbed.

Since $\sigma_s\Delta\theta$ and $\sigma_l\Delta\theta$ are both small compared with l, their difference may be neglected in comparison with l, and we have for the heat *absorbed* in the cycle l, at a temperature θ, and for the net work performed

$$p(v_2-v_1)-(p-\Delta p)\,(v_2-v_1)=(v_2-v_1)\,\Delta p$$

The thermodynamic efficiency of the process carried out is therefore

$$\frac{(v_2-v_1)\,\Delta p}{l},$$

and the temperature limits are θ and $\theta-\Delta\theta$. The importance of Carnot's theorem now becomes evident; we can equate the above value to the value we found for the efficiency of the perfect gas cycle between the same temperature limits, since all reversible 'heat engines' have the same efficiency. The efficiency of the perfect gas cycle would be

$$\frac{\theta-(\theta-\Delta\theta)}{\theta} \quad \frac{\Delta\theta}{\theta}$$

Whence we have $\frac{\Delta p}{l}(v_2-v_1)=\frac{\Delta\theta}{\theta}$.

or $$\frac{\Delta\theta}{\Delta p}=\frac{\theta(v_2-v_1)}{l}$$

This is an important relation connecting the change of melting point with pressure, the latent heat of fusion, and the difference between the specific volumes of the two phases

This relation could not have been arrived at without the aid of the theorem stating that all reversible heat engines have the same efficiency We therefore proceed to prove this theorem

PROOF OF CARNOT'S THEOREM

The theorem is established by showing that if all reversible engines had not the same efficiency when working between the same temperature limits then the Second Law of Thermodynamics would be untrue

Let an engine *A* have a greater efficiency than another reversible engine *B* working between the same temperature limits θ_1 and θ_2 Although the efficiencies are assumed to be unequal, the two engines may be arranged so that equal amounts of work are performed in a cycle of each merely by adjusting in an appropriate way the amounts of substance taken, that is by making the less efficient engine relatively larger Let the two engines be coupled together so that the more efficient one works the less efficient one backwards, i e one expands and does work on the other at the higher temperature, and vice versa at the lower temperature During each complete cycle *A*, the more efficient, draws a quantity of heat Q_1 from a source at the higher temperature θ_1, and rejects Q_2 at θ_2, while *B*, the less efficient, which is being driven backward, rejects Q_1' at θ_1 and absorbs Q_2' at θ_2 Were it working direct it would of course absorb Q_1' at θ_1 and reject Q_2' at θ_2

Since the engines are arranged to perform equal amounts of work in a complete cycle, *B* in being driven backward requires just the amount of work which *A* can supply No work is therefore available for external use; nor, however, is any required to keep the combination just in action We have

Q_1-Q_2(≡work performed by *A*)$=Q_1'-Q_2'$(≡work performed on *B*)

But $$\frac{Q_1-Q_2}{Q_1} > \frac{Q_1'-Q_2'}{Q_1'},$$

since A is more efficient than B.

Therefore $$Q_1' > Q_1$$
and $$Q_2' > Q_2$$

$Q_1'-Q_1$ is therefore positive Q_1' is the heat which B gives to the high temperature source, and Q_1 is the heat which A takes from the same source Therefore a net positive quantity of heat $Q_1'-Q_1$ has been yielded to the high temperature source

Also $Q_2'-Q_2$ is positive This represents the excess of the heat taken by B from the low temperature source of heat over that returned by A to the same source

As a net result of the cycle, therefore, heat has been removed from a body at a lower temperature and yielded up to a body at a higher temperature, while no work has been performed on the system which, moreover, is in exactly the same state at the end of the cycle as at the beginning This is not in accordance with the second law of thermodynamics We must therefore conclude that it is impossible to find two reversible engines with different efficiencies, and that Carnot's theorem is true.

It should be noted that the above cycle involved nothing out of keeping with the first law because the quantity of heat $Q_2'-Q_2$, withdrawn from the low temperature reservoir, was exactly equal to the quantity $Q_1'-Q_1$, yielded up to the high temperature reservoir, since $Q_1-Q_2=Q_1'-Q_2'$

V Having arrived at the result that the function $\frac{Q_1-Q_2}{Q_1}$ must be the same for all reversible processes which we can imagine to take place in a cyclical manner, Q_1 being absorbed at θ_1 and Q_2 rejected at θ_2, we proceed to evaluate $\frac{Q_1-Q_2}{Q_1}$ in some simple case The result obtained will, by Carnot's theorem, be quite general, and not limited to the special case for which it is originally derived.

The simplest case in which to evaluate $\frac{Q_1-Q_2}{Q_1}$ is that of a perfect gas traversing Carnot's cycle. Since our fundamental temperature scale is the perfect gas thermometer scale, we arrive at a very simple form of result in this instance,

namely,
$$\frac{Q_1-Q_2}{Q_1}=\frac{\theta_1-\theta_2}{\theta_1}$$

The calculation is as follows

Referring back to section I, we have

$$Q_1=\int_{v_1}^{v_2} p\,dv=R\theta_1\,ln\frac{v_2}{v_1},$$

$$Q_2=\int_{v_4}^{v_3} p\,dv=R\theta_2\,ln\frac{v_3}{v_4}$$

Therefore
$$\frac{Q_1-Q_2}{Q_1}=\frac{R\theta_1\,ln\frac{v_2}{v_1}-R\theta_2\,ln\frac{v_3}{v_4}}{R\theta_1\,ln\frac{v_2}{v_1}},$$

but, since A and B, and C and D are on the same isothermals,

$$\left.\begin{array}{l}p_1v_1=p_2v_2\\ p_3v_3=p_4v_4\end{array}\right\}$$

Also, since A and D, and B and C are on the same adiabatics,

$$\left.\begin{array}{l}p_1v_1^{\gamma}=p_4v_4^{\gamma}\\ p_2v_2^{\gamma}=p_3v_3^{\gamma}\end{array}\right\}$$

From these four relations it follows that

$$\frac{v_2}{v_1}=\frac{v_3}{v_4}.$$

$$\frac{Q_1-Q_2}{Q_1}=\frac{\theta_1\,ln\frac{v_2}{v_1}-\theta_2\,ln\frac{v_3}{v_4}}{\theta_1\,ln\frac{v_2}{v_1}}=\frac{\theta_1-\theta_2}{\theta_1}$$

The simplicity of this result may at first perhaps be regarded as surprising For we know that it must be true in every case, no matter how complicated the system to which it is applied, although its derivation depended upon the special equations of a perfect gas The explanation of any difficulty which may be felt in this respect lies in remembering that θ_1 and θ_2 remain in all cases the temperatures as measured by the perfect gas thermometer The simplicity of the result depends upon our having chosen for the evaluation of the efficiency that system which is also the standard of temperature measurement

To summarise, therefore, the means by which the Second

Law of Thermodynamics is applied, we begin by imagining some physical or chemical process carried out in a cyclical manner, taking place in one direction with absorption of heat at a higher temperature and subsequently being reversed at a lower temperature with rejection of a fraction of this heat originally absorbed The device employed, however impracticable it may be, is termed a heat engine

We define the efficiency of any heat engine as the ratio

$$\frac{\text{work performed in cycle}}{\text{heat drawn from supply}}$$

It is demonstrated in Carnot's theorem that this function must have the same value for *all* reversible heat engines, for otherwise the Second Law of Thermodynamics could not be true

We now proceed to evaluate the efficiency in the simple case of a perfect gas traversing a Carnot cycle, and find it to be $\frac{\theta_1-\theta_2}{\theta_1}$ Carnot's theorem shows that this result must be quite general By equating the efficiency calculated in the specific case of some particular cycle to this general value, important laws governing the physical or chemical processes upon which the cycle is based are derived as in the example given relating to fusion and solidification

The validity of the results which are found by this method is in no way restricted by the fact that in deriving them assumptions are made about processes taking place in an ideal manner In practice, naturally, no cycle could be carried out in a strictly reversible manner gases would have to be expanded or compressed at a finite rate, a body could not draw heat from a reservoir at the same temperature as itself to replenish that which it lost in the performance of work, it would have, rather, to cool a little, and then receive heat from the reservoir now at a slightly higher temperature than itself. But all these factors only make the actual efficiency less than the thermodynamic efficiency $\frac{\theta_1-\theta_2}{\theta_1}$. The ideal cycle, conceived only, provides a means by which relations between various physical properties are derived These relations are quite independent of the intellectual scaffolding by the aid of which they are discovered

We must now return to consider more closely the conditions determining the reversibility of a change, and the special properties of a reversible change In a reversible process there is equilibrium at every stage This means that only processes which proceed very slowly can be approximately reversible It is only in such processes that the maximum amount of external work can be performed An example will make this clear Considering once more the isothermal expansion of a gas, if the gas pressure is p, and the opposing pressure against which the gas is expanding is $p-dp$, the work performed during an expansion dv, differs infinitely little in the limit from pdv, and for a finite expansion from volume v_1 to v_2, during which the external pressure is gradually relaxed from a value differing infinitely little from the initial gas pressure p_1, to a value p_2, equal to the final gas pressure, the integral work performed for one gram molecule of the gas is, as we have seen, $R\theta \, ln\frac{v_2}{v_1}$ The process could be reversed at any moment by increasing the opposing pressure by an infinitesimal amount and the work pdv, performed by the gas on expansion would be replaced by an amount of work pdv, performed on the gas by the external pressure during compression

If instead of the external pressure being continuously lowered so as to be an equilibrium pressure at each point it were suddenly lowered to the final value p_2, the gas would expand to the volume v_2, corresponding to p_2, but throughout the expansion the external pressure, in overcoming which work is performed, has the constant value p_2, so that the whole work done between the limits of expansion, v_2-v_1, equals $p_2(v_2-v_1)$ This is less than the work done during the reversible expansion, as may be clearly seen from the figure in which the area $ABQP$ represents the work done in the reversible expansion and A^1BQP that in the irreversible expansion

At the risk of labouring the point, let us compare the two processes during the first element of the change In the reversible one the work done is p_1dv, while the work necessary to reverse the operation is p_1dv also In the irreversible one the work done is p_2dv, whilst that necessary to reverse the operation is not p_2dv but the larger amount p_1dv The difference between the maximum work obtainable, p_1dv, and that actually obtained, p_2dv, is $(p_1-p_2)dv$ If there are no frictional forces retarding the outward movement of the piston this excess of energy appears as mass kinetic energy of gas and piston When the limit of expansion is reached, the gas and piston, which are moving with finite velocity, must be brought to rest, and the kinetic energy will be dissipated as heat Had the operation been conducted reversibly an

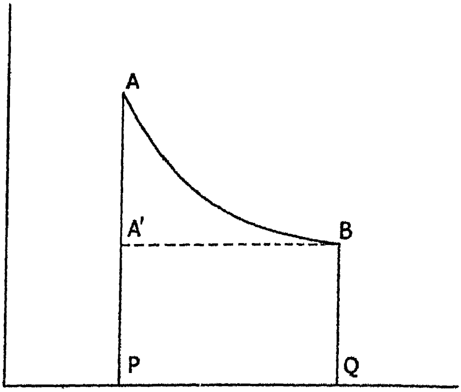

FIG 2

equal amount of energy might have appeared in the form of external mechanical work Where frictional forces oppose the expansion a finite difference of pressure is necessary to produce expansion or compression Hence the operation is unavoidably irreversible, and some energy must be dissipated as heat, on account of the work done in overcoming the frictional forces, in whichever direction the change proceeds This again diminishes the yield of work from an irreversible operation as compared with a reversible one

Another kind of irreversibility may be illustrated by reference to the cycle which gave the influence of pressure on the melting point of a solid One of the operations in this cycle was the fusion of the substance at the melting point corresponding to a given external pressure At this temperature solid and liquid are in equilibrium This is the important point because it determines the reversibility of the process By the addition of an infinitesimally small quantity of heat some solid may be caused to melt, whilst by the withdrawal of an infinitesimally small quantity of heat a proportional amount of liquid is caused to solidify This could not happen if the temperature were any other than the equilibrium temperature If it were higher the whole of the solid would melt irreversibly, and the withdrawal of an infinitesimal amount of heat would not cause any of the substance to freeze again, if it were lower the whole of the liquid would solidify irreversibly When the pressure on the system is changed, the temperature must be varied in a corresponding way so that it always remains the equilibrium value In this way the cycle can be carried out reversibly, and we obtain our relation between pressure and the temperature at which solid and liquid are in equilibrium, that is, the melting point

When heat is drawn from or given to a reservoir, as in the isothermal operations of Carnot's cycle, reversibility demands thermal equilibrium between source and recipient, that is to say, equality of temperature between the gas and the heat reservoir Naturally, the flow of heat from one to the other can take place only infinitely slowly under these conditions

At this stage it will be convenient to call attention to an important rider which we shall need to develop and apply later Since a process can only be reversible when equilibrium conditions prevail at every stage, a criterion of a condition of equilibrium is that any small change from it which is made shall be a reversible change This has an important application in connection with the use of thermodynamic functions

CHAPTER IV

THE GIBBS-HELMHOLTZ EQUATION, MAXIMUM WORK, AND FREE ENERGY

We have seen in two examples how physical processes can be carried out in a reversible and cyclic manner, and thereby made to constitute heat engines The application of the Second Law of Thermodynamics to determine the efficiency of these heat engines leads to the discovery of important laws which the various processes obey To illustrate further the characteristics of these so-called heat engines, we will first consider another specific example of such a cyclic process, and then proceed to derive a general equation which applies to all physical and chemical changes

The process which will be taken as the basis of the cycle will be the vaporisation of a liquid It will be instructive to compare each step of this cycle with the analogous step of the Carnot cycle with a perfect gas

(1) One gram of the liquid is allowed to vaporise reversibly at temperature θ This corresponds to the isothermal expansion of the gas at θ_1 in Carnot's cycle, an amount of heat l, equal to the latent heat of ~~fusion~~ vaporisation, is absorbed, and work is performed against external pressure during the expansion which accompanies the vaporisation l thus corresponds to the Q_1 of the Carnot cycle It is very important now to consider under what conditions the vaporisation can occur reversibly, the condition for reversibility is that the liquid and vapour should be in equilibrium or infinitely little removed from equilibrium at every stage This, clearly, can only happen if the external pressure to be overcome by the vaporisation of the liquid is always kept equal to the saturated vapour pressure of the liquid, we say equal as the limiting case, since for the process actually to occur the opposing pressure would have to be reduced to a value very slightly below the vapour pressure There is now an important difference between this example and the case of the expanding gas In the latter case the equilibrium pressure falls in accordance with Boyle's law as the volume increases,

but in the case of the vaporising liquid the pressure remains constant and equal to the vapour pressure, for the vapour pressure of a liquid does not depend in any way on the relative volumes of liquid and vapour At constant temperature it is constant If we imagine the liquid to be enclosed in a cylinder fitted with a piston, the space over the liquid being occupied by the pure vapour, then the pressure exerted by the vapour remains at a constant value p, no matter how far the piston moves out (provided that all the liquid is not used up) The work done in the reversible vaporisation of 1 gram of the liquid is therefore $\int p dv = p(v_2 - v_1)$ where $v_2 =$ volume of 1 gram of vapour, and $v_1 =$ volume of 1 gram of liquid at the temperature θ

Another difference must now be noted between the vaporisation process and the expansion of the perfect gas The internal energy of the perfect gas has been shown to be independent of the volume, and therefore the whole of the heat Q_1, absorbed by the gas during its expansion, was handed on for the performance of external work In the vaporisation, however, only a part of the latent heat is utilised for the overcoming of the external pressure, the rest going to increase the internal energy of the substance vaporised Vapour, as already pointed out, has a larger internal energy than liquid, because work has been employed in separating the molecules against their mutual attractions, and thus increasing the potential energy This is only pointed out as a fact, it does not in the least destroy the analogy between the l of this cycle and the Q_1 of the gas cycle, because the very basis of the investigation is the sure knowledge, derived from Carnot's theorem, that the efficiency function will have the same value whatever be the nature of the process upon which the heat engine depends

To sum up, then, we have for this first isothermal process at θ

$$\text{Heat absorbed} = l$$
$$\text{External work performed} = p(v_2 - v_1)$$

(ii) It is now necessary to reduce the temperature to $\theta - d\theta$ with a view to reversing the process at this lower temperature A simple adiabatic expansion does not meet the case completely, because although we should in this way reduce the temperature to $\theta - d\theta$, the pressure corresponding to this new temperature would not necessarily be the equilibrium pressure, i e the vapour pressure at $\theta - d\theta$ We must therefore imagine a slight adiabatic expansion followed by a small isothermal expansion or compression to bring the vapour to the saturation point This small change can be regarded as forming part of stage (iii)—the isothermal stage —but it is more convenient to deal with it at once Any heat taken in or rejected will be an infinitesimal quantity of the first order The new volume of the vapour is $v_2-\frac{\partial v_2}{\partial\theta}d\theta$, where $\frac{\partial v_2}{\partial\theta}$ is the rate of change with temperature of the specific volume of the saturated vapour There has thus been a contraction of $\frac{\partial v_2}{\partial\theta}d\theta$, which has occurred under a pressure varying between p and $p-dp$ There has thus been work done on the system equal to the average pressure multiplied by the volume change Since the average pressure is $p-h\,dp$, where h is a fraction nearly equal to $\frac{1}{2}$, this work is $(p-h\,dp)\frac{\partial v_2}{\partial\theta}d\theta$, or, neglecting quantities of the second order, $p\frac{\partial v_2}{\partial\theta}d\theta$

(iii) We now condense the 1 gram of vapour reversibly at the new vapour pressure $p-dp$ The work done on the system by the external pressure causing the condensation is

$$(p-dp)\times \text{volume change}$$

$$=(p-dp)\left[\left(v_2-\frac{\partial v_2}{\partial\theta}d\theta\right)-\left(v_1-\frac{\partial v_1}{\partial\theta}d\theta\right)\right]$$

Neglecting once more second order infinitesimals, this becomes

$$(p-dp)\,(v_2-v_1)\quad p\left(\frac{\partial v_2}{\partial\theta}d\theta-\frac{\partial v_1}{\partial\theta}d\theta\right)$$

The heat rejected in this stage is $l-dl$

(iv) The condensed liquid is now warmed to θ once more, the pressure being increased to the original value p. In this stage a quantity of heat is taken in which is an infinitesimal of the first order, external work is done by the expansion of the liquid to its original volume v_1, from the volume $\left(v_1-\frac{\partial v_1}{\partial\theta}d\theta\right)$ which it possessed at the lower temperature This work is $p\frac{\partial v_1}{\partial\theta}d\theta$, neglecting only the second order terms (approximately equal to $\frac{1}{2}dp\,d\theta\frac{\partial v_1}{\partial\theta}$)

The net work performed by the system in this cycle is $(v_2-v_1)dp+$terms of the second order.

For the terms involving $\frac{\partial v_2}{\partial \theta}$ and $\frac{\partial v_1}{\partial \theta}$ in (ii) and (iv), cancel those in (iii), thus the term $+p\frac{\partial v_2}{\partial \theta}d\theta$, representing work done *on* the system in (ii) is cancelled by the term $-p\frac{\partial v_2}{\partial \theta}d\theta$ for work done *on* the system in (iii), and the term $+p\frac{\partial v_1}{\partial \theta}d\theta$ for work done *by* the system in (iv) is cancelled by the term $+p\frac{\partial v_1}{\partial \theta}d\theta$ for work done *on* the system in (iii) It makes absolutely no difference what sign the actual values of $\frac{\partial v_1}{\partial \theta}$ and $\frac{\partial v_2}{\partial \theta}$ possess We have spoken as though they were positive, but since positive work done *on* a system equals negative work done *by* a system this convention did not involve any arbitrary assumption

Now, the heat drawn from the supply at the higher temperature θ is l, except for small quantities of the first order in (iv), which vanish in comparison with the finite quantity l

Thus, the efficiency $=\frac{(v_2-v_1)dp}{l}$.

$$=\frac{\theta-(\theta-d\theta)}{\theta}=\frac{d\theta}{\theta}$$

Therefore $$\frac{dp}{d\theta}=\frac{l}{\theta(v_2-v_1)}$$

This gives the rate of variation with temperature of the saturated vapour pressure

We have discussed the various stages in some detail because there is sometimes a little difficulty in knowing which of the infinitesimal terms in such a calculation may be neglected

It will be seen that since, in the efficiency function, the heat term is finite, heat terms which are infinitesimals of the first order may be neglected The work term, however, in a cycle in which the temperature difference is only an infinitesimal of the first order is itself an infinitesimal of the first order Thus, it is only permissible to neglect work terms which are infinitesimals of the second or higher order

The whole derivation may be summarised in the diagram below.

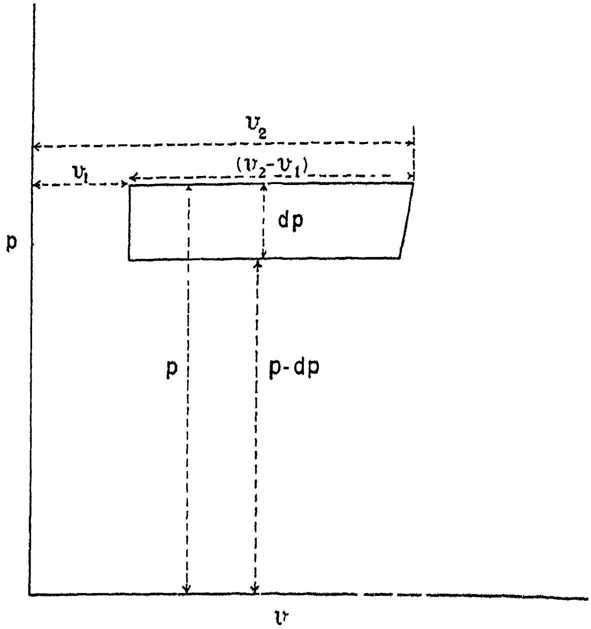

FIG 3.

Total work done in cycle = area enclosed by p,v diagram $=(v_2-v_1)dp$, *neglecting second order quantities*

$$\text{Efficiency} = \frac{d\theta}{\theta} = \frac{(v_2-v_1)dp}{l}.$$

THE CLAUSIUS EQUATION

The volume of a liquid being small compared with that of a vapour at the same temperature and pressure, we may write

$$\frac{dp}{d\theta} = \frac{l}{(v_2-v_1)\theta} = \frac{l}{v_2\theta}.$$

Multiplying by M the molecular weight of the substance in the vapour state, we have

$$\frac{dp}{d\theta} = \frac{Ml}{Mv_2\theta} = \frac{L}{V\theta}.$$

where L is the molecular latent heat, and V the molecular volume of the vapour If the vapour obeys Boyle's law,

$$pV=R\theta, \text{ thus } V=\frac{R\theta}{p},$$

$$\frac{dp}{d\theta}=\frac{Lp}{R\theta^2},$$

$$\frac{1}{p}\frac{dp}{d\theta}=\frac{L}{R\theta^2},$$

$$\frac{d\,ln\,p}{d\theta}=\frac{L}{R\theta^2}$$

A GENERALISED CYCLE CONSTANT VOLUME RELATIONSHIP

The foregoing discussion having exemplified the more important points connected with cyclic processes, it will now be possible to carry out a generalised form of cyclic process without undue obscurity

A physico-chemical process in general, taking place at a temperature θ, is accompanied by a diminution in total internal energy U, of the substance or substances which undergo the change, the absorption of an amount of heat Q, and the performance of an amount A of external work According to the specific nature of the change, and the sense in which it occurs, U, Q, and A may be positive, negative, or zero When the process takes place in a reversible manner A is the maximum work obtainable In the rest of this discussion A will be used in this sense of the maximum work. When the process is the expansion of a perfect gas we have seen that $U=0$, the internal energy does not change and Q, the heat absorbed, is equal to A, the external work performed When the process is the vaporisation of a liquid, Q, the heat absorbed, is the total latent heat, A is the work done against the external pressure (equal to the vapour pressure), and U is the change in total internal energy Since we are calling a diminution positive, the value of U for the process of vaporisation occurring in the sense liquid→vapour will be negative

We have that the heat absorbed, Q, is utilised partly in increasing the internal energy, the *increase* being $-U$ and partly in enabling the system to perform external work, A In general, therefore, $Q=-U+A$

In some cases A may be zero, as, for example, in the reversible fusion of a solid when the specific volumes of solid and liquid are equal Here $Q=-U$, i e all the latent heat is used in furnishing the increased internal potential energy of the liquid

The external work may be of many kinds It is not in general accounted for merely by the expansion of the system during the transformation During the working of a galvanic cell much external work is done, scarcely any of which is work of expansion Indeed, if the initial and final volumes of the system are equal, the work of expansion is necessarily zero whatever be the nature of the transformation We shall have numerous examples of different kinds of external work in what follows It will be a convenience to differentiate between work of expansion and other work Let us call A_p the total work including an expansion from volume v_1 to volume v_2 against a constant external pressure p, then the work other than that done in overcoming this pressure is

$$A_p-p(v_2-v_1)=A_v$$

When $v_2=v_1$ this reduces to $A_p=A_v$

We will first consider the simplest possible case, namely, when $A=A_v$, there being no volume change in the transformation

We allow our isothermal process to take place at θ, Q being absorbed and external work A_v performed

$$Q=A_v-U$$

The system is now cooled to $\theta-d\theta$, the volume being kept constant An infinitesimal amount of heat is abstracted in this process, which, however, is negligible in comparison with Q No work is done, but the pressure has had to be reduced in order that the volume may remain constant.

The process is now reversed at the temperature $\theta-d\theta$ $Q-dQ$ is rejected, the internal energy change is $-(U-dU)$, and the work done on the system is A_v-dA_v

The system is now warmed to θ once more, everything being restored to the initial state; the pressure is brought to its original value

The efficiency of the process as we have carried it out is

$$\frac{\text{work done}}{\text{heat taken in}}=\frac{A_v-(A_v-dA_v)}{Q},$$

$$=\frac{dA_v}{A_v-U},$$

since $A_v-U=Q$,

Therefore
$$\frac{dA_v}{A_v-U}=\frac{d\theta}{\theta},$$
$$A_v-U=\theta\frac{dA_v}{d\theta}$$

The value of dA_v is $\left(\frac{\partial A_v}{\partial\theta}\right)_v d\theta$, since the condition of the transformation at $\theta-d\theta$ was such that both initial and final volumes were not only equal to each other, but also to the initial and final volumes at θ

We thus have $$A_v-U=\theta\left(\frac{\partial A_v}{\partial\theta}\right)_v$$

It may save some confusion later if it is pointed out that in the expression $\left(\frac{\partial A_v}{\partial\theta}\right)_v$ the two subscript v's are independent, A_v indicates that the transformation at θ is carried out at constant volume, whilst $\left(\frac{\partial}{\partial\theta}\right)_v$ indicates that the constant volume transformation at $\theta-d\theta$ is carried out at the *same* constant volume as before It would have been possible to allow the change to take place at constant volume at θ, to cool under constant pressure, allowing the system to contract naturally, then to reverse the change at the new constant volume This would correspond to $\left(\frac{\partial A_v}{\partial\theta}\right)_p$

There is no difficulty about the matter, it is only necessary to be clear about what we really mean by the *same* change at different temperatures

The equation $A_v-U=\theta\left(\frac{\partial A_v}{\partial\theta}\right)_v$ is a most important one, and is known as the Gibbs-Helmholtz equation

For many of the systems with which we shall have to deal the conditions of volume constancy are exactly or very nearly fulfilled, so that this equation may be applied directly Even when the volume cannot be regarded as constant it is always easy to correct the total work for the expansion term, and then apply the equation to this corrected value In the next section the corresponding constant pressure relation will be discussed, but for examples of the significance of the Gibbs-Helmholtz equation reference should be made at once to the next section but one

We shall now write the equation simply in the form

$$\mathbf{A}-\mathbf{U}=\theta\frac{d\mathbf{A}}{d\theta}.$$

MAXIMUM WORK AT CONSTANT PRESSURE

Let constant pressure prevail throughout the cycle during heating and cooling as well as during the isothermal stages

(i) The process takes place at θ The work performed, $A_p=A_v+p(v_2-v_1)$ $Q=A_p-U$ taken in

(ii) The system is cooled to $\theta-d\theta$ The heat terms are infinitesimals of the first order The pressure remains constant v_2 diminishes to $v_2-\frac{\partial v_2}{\partial\theta}d\theta$

Therefore work is done on the system equal to $p\frac{\partial v_2}{\partial\theta}d\theta$

(iii) The process is reversed at $\theta-d\theta$ Work A_p-dA_p is done on the system

(iv) The system is warmed to θ again The volume increases from $v_1-\frac{\partial v_1}{\partial\theta}d\theta$ to v_1, so that the system does work equal to $p\frac{\partial v_1}{\partial\theta}d\theta$

The total work done by the system is therefore

$$A_p-(A_p-dA_p)+p\frac{\partial v_1}{\partial\theta}d\theta-p\frac{\partial v_2}{\partial\theta}d\theta,$$

$$=dA_p-p\frac{\partial(v_2-v_1)}{\partial\theta}d\theta$$

Efficiency $$=\frac{dA_p-p\frac{\partial(v_2-v_1)}{\partial\theta}d\theta}{A_p-U}=\frac{d\theta}{\theta}.$$

Therefore $A_p-U=\theta\left[\frac{\partial A_p}{\partial\theta}-p\frac{\partial(v_2-v_1)}{\partial\theta}\right]$,

since $dA_p=\frac{\partial A_p}{\partial\theta}d\theta$

Thus $A_p-U=\theta\frac{\partial\{A_p-p(v_2-v_1)\}}{\partial\theta}$, but $A_p - p(v_2 - v_1)$ is the work that would be done if the expansion were suppressed during the isothermal stages

Thus
$$A_p - U = \theta\left(\frac{\partial A_v}{\partial\theta}\right)_p,$$
or
$$A_v - U + p(v_2 - v_1) = \theta\left(\frac{\partial A_v}{\partial\theta}\right)_p$$

This equation could have been written down by applying the appropriate corrections to the constant volume equation of the last section It may clarify matters to do this now

Let the process in which volume changes had been suppressed, and which satisfied the equation $A_v - U = Q = \theta\left(\frac{\partial A_v}{\partial\theta}\right)_v$ now take place with volume change, A_v remaining the same An extra amount of heat $p(v_2 - v_1)$ must be taken in Thus Q must be increased from $A_v - U$ to $A_v - U + p(v_2 - v_1)$ Of the total work the portion A_v is the same whether there is work of expansion or not Hence $\left(\frac{\partial A_v}{\partial\theta}\right)_v$ is the same as $\left(\frac{\partial A_v}{\partial\theta}\right)_p$ Thus the equation $A_v - U = Q = \theta\left(\frac{\partial A_v}{\partial\theta}\right)_v$ is changed to $A_v - U + p(v_2 - v_1) = \theta\left(\frac{\partial A_v}{\partial\theta}\right)_p$

This equation is concerned with that part of the external work not involved in expansion If interest is fixed on the total work A_p, it is to be noted that the term $\left(\frac{\partial A_p}{\partial\theta}\right)_p$ means that the process at different temperatures must always take place under the same pressure and therefore between *different volume limits*

The process with which A is associated however may be such that it is not convenient to regard p as constant at different temperatures If we are considering the evaporation of a liquid, for example, under its own vapour pressure, this is indeed a change at constant pressure, but the constant pressure which prevails during the isothermal change is one having a different value at each temperature

Let us consider briefly a cycle in which the isothermal changes are at constant pressure, but in which the pressure cannot be arbitrarily varied and has to have a definite value determined by the temperature v_2 and v_1, the final and initial volumes of the system in the isothermal transformation, will themselves vary with temperature in this case

(i) The process takes place at θ The work done by the system is $A_p=A_v+p(v_2-v_1)$ The heat taken in is $Q=A_p-U$

(ii) The system is cooled to $\theta-d\theta$ The heat terms involved are infinitesimals of the first order, vanishing in comparison with Q

The volume v_2 becomes $\left(v_2-\frac{\partial v_2}{\partial\theta}d\theta\right)$ Work is done on the system equal to $p\frac{\partial v_2}{\partial\theta}d\theta$, neglecting second order quantities arising from the fact that the average pressure is not p but between p and $p-dp$

(iii) The process is reversed at $\theta-d\theta$ The work done on the system is

$$A_p-dA_p=A_v-dA_v+(p-dp)\left\{\left(v_2-\frac{\partial v_2}{\partial\theta}d\theta\right)-\left(v_1-\frac{\partial v_1}{\partial\theta}\right)\right\}$$

(iv) The system is warmed up to θ again The pressure returns to the value p The volume increases from $v_1-\frac{\partial v_1}{\partial\theta}d\theta$ to v_1. Work is done by the system equal to $p\frac{\partial v_1}{\partial\theta}d\theta$, again omitting second order quantities

Adding up all the work terms we obtain for the net work done by the system

$$dA_v+dp(v_2-v_1)$$

Therefore

$$\frac{dA_v+dp(v_2-v_1)}{A_p-U}=\frac{d\theta}{\theta}.$$

$$A_p-U=\theta\left\{\frac{dA_v}{d\theta}+\frac{dp}{d\theta}(v_2-v_1)\right\}.$$

Now since $A_p=A_v+p(v_2-v_1)$, the expression in the bracket on the right hand side of the equation is the differential coefficient of A_p with respect to temperature subject to the condition that (v_2-v_1) is regarded as constant in the actual performance of the differentiation Thus we may write for this case

$$A_p-U=\theta\left(\frac{\partial A_p}{\partial\theta}\right)_{v_1v_2}$$

It is understood that v_1 and v_2 were not forced to remain constant when the temperature was lowered in the cycle, but in the final equation they must be treated as independent of temperature

In this form the equation can be applied to such processes as vaporisation We may illustrate its use by considering this particular example .

$$A_p=p(v_2-v_1),$$

$$Q=A_p-U=l\,,\ \text{whence}\ U=p(v_2-v_1)-l\,;$$

$$\left(\frac{\partial A_p}{\partial\theta}\right)_{v_1v_2}=(v_2-v_1)\frac{dp}{d\theta}$$

$$\text{Therefore if}\ A_p-U=\theta\left(\frac{\partial A_p}{\partial\theta}\right)_{v_1v_2},$$

$$l=\theta\,(v_2-v_1)\frac{dp}{d\theta},$$

$$\frac{dp}{d\theta}=\frac{l}{\theta(v_2-v_1)}$$

FREE ENERGY

After this digression we return to the main argument

The quantity A, the external work performed when any physical or chemical process is carried out reversibly at constant temperature, is of great importance As we have seen, it can often be expressed as the sum of two terms one representing the work of expansion, the second work done in other ways If the volume of the system is unchanged at the end of the process, then the quantity A is represented by the second term only A is called the decrease in *Free energy* of the system The system, having done work A, is thought of as being by that much less endowed with this property called free energy There is a slight confusion about the use of this term as it is sometimes applied rather to the total work less the work of expansion All that matters, however, is to be clear about the facts We shall use the term in the sense in which it was originally introduced, namely, the maximum work at constant temperature

GALVANIC CELLS

The subject of Free Energy may conveniently be developed by reference to the important question of the electromotive force of a galvanic cell A galvanic cell is an arrangement whereby the chemical energy of certain substances is utilised for the production of electrical energy. Two examples will serve to bring out the points relevant to the thermodynamical discussion.

In the Daniell cell zinc dissolves at the negative pole yielding zinc sulphate, and copper is deposited at the positive pole, the chemical process being $Zn+CuSO_4=ZnSO_4+Cu$, or, as it is more precisely expressed in terms of the ionic theory, $Zn+\overset{++}{Cu}=\overset{++}{Zn}+Cu$. If this change, the precipitation of copper by zinc, merely took place in a calorimeter, the solutions no longer being separated as in the cell, there would be a certain evolution of heat which would represent the decrease in total internal energy of the substances reacting. When the precipitation takes place in a calorimeter there is no means of reversing the process by a slight change in the conditions. The process is irreversible in the thermodynamic sense (this, it need hardly be pointed out, has nothing to do with the question of whether the process is a reversible reaction in the chemical sense). No external work accompanies this precipitation.

On the other hand when the change occurs under the conditions prevailing in the cell, the change is reversible, because we know that by applying to the cell a reverse electromotive force slightly greater than its own, the copper can be caused to dissolve and the zinc to be precipitated. Moreover, when the chemical process occurs reversibly in the cell it yields external work. When one gram equivalent of zinc dissolves a quantity of electricity equal to 96,540 coulombs flows through the cell and the external circuit, and the movement of 96,540 coulombs through a difference of potential E, the e.m.f. of the cell, represents the performance of 96,540 E electrical units of work, which are completely convertible into mechanical work of any other kind.

Another interesting case is the oxygen-hydrogen cell. This consists essentially of two electrodes of platinum, charged respectively with oxygen and hydrogen, dipping into water. The chemical process consists in the passage of hydrogen and oxygen into solution in the ionic form, and then union to form water. The change in total energy accompanying this process is simply that of the reaction $2H_2+O_2=2H_2O$ and is measured by the heat which would be evolved if the gases were made to combine at constant volume in a bomb calorimeter (corrected for the latent heat of condensation of the steam if necessary) The combination of hydrogen and oxygen to form water by explosion in a calorimeter is an irreversible process in the thermodynamic sense, and does not yield work The whole of the internal energy change appears as heat But the operation of the hydrogen-oxygen cell is a reversible process when allowed to proceed against a back electromotive force only very slightly less than its own, and external work may be obtained The amount is numerically equal to the electromotive force multiplied by the quantity of electricity passing This is proportional, by Faraday's law, to the amount of chemical action which has occurred When the cell works it should be observed that the amount of heat actually liberated during the working is not the same as that which is liberated when the same chemical reaction takes place in a calorimeter without the performance of any work The change in total internal energy of the substance is of course the same, but it does not appear entirely as heat Some appears as electrical energy, which may be utilised in the performance of mechanical work The amount of heat actually liberated in the cell is equal to the difference between the total energy change and the external work When the reaction takes place in the constant volume calorimeter the heat of reaction is the whole change in total internal energy

The Gibbs-Helmholtz equation can be appropriately applied to the electrical process, any volume changes accompanying the working of cells being negligible, or it being supposed that correction is made for them The change in total internal energy, U, is given by the heat of reaction at constant volume, that is the heat which would be liberated if the chemical reaction upon which the cell depends, took place without performance of external work (*not* the actual heat which may be liberated or absorbed in the cell itself)

A, the free energy change, is proportional to the electromotive force, E, of the cell, because the work which the cell can perform at constant temperature is given by ECt, where Ct is the total quantity of electricity which passes during the process This quantity may be readily found from Faraday's law In the Daniell cell, for example, if U, the internal energy change, refer to one gram molecule of copper or zinc, then the quantity of electricity passing will be $2F$, where F is 96,540 coulombs, which are always associated with a univalent gram ion The factor 2 comes from the divalency of copper and zinc. In general for n-valent ions the quantity is nF. A, therefore, is nEF, and $\frac{dA}{d\theta}$ is $nF\frac{dE}{d\theta}$.

The general equation thus becomes

$$nEF - U = \theta\, nF\frac{dE}{d\theta}.$$

E is usually measured in volts, F in coulombs. nEF will therefore be in volt-coulombs. 1 volt-coulomb $= 10^8 \times 10^{-1} = 10^7$ ergs.

Therefore to convert to calories, nEF in volt-coulombs is multiplied by 10^7 and divided by $4{\cdot}18 \times 10^7$. The same conversion must be made with the term, $nF\frac{dE}{d\theta}$.

U will be now measured in calories per gram molecule.

We must now consider the question of the strict reversibility of the process. Upon it the validity of the equation will depend. The electromotive force of a cell may be used in two ways, in yielding current against the internal and external resistance, and in overcoming an opposing potential difference. The latter alone yields useful work; the opposing potential difference might, for example, be the back electromotive force of a motor. A cell cannot work reversibly if it yields a finite current; energy is dissipated as heat (Joule heat) both when it works directly, and when it is made to work backwards by the application of a greater and opposed electromotive force. Moreover a finite increase in the opposing potential difference would be necessary to cause the reversal of the current. If, however, the cell yields a vanishingly small current against an opposing electromotive force only very slightly smaller than its own—e.g., drives a motor infinitely slowly—then the process becomes as nearly reversible as we like. Although the cell cannot, under these conditions, function to any practical purpose, yet these conditions are precisely those under which we measure the electromotive force. The potentiometric method depends upon finding the opposing potential difference which will just prevent the cell from giving a current. The electromotive force of the cell is thus determined under just those equilibrium conditions which represent the limiting case of the truly reversible process. It measures the tendency of the cell to yield work, when the cell actually works it yields rather less than the maximum indicated by its electromotive force, as some of the energy is reconverted into heat in overcoming the internal resistance of the cell itself, and the potential difference between the terminals of the cell is less than the true electromotive force by this amount. But the true electromotive force, as measured potentiometrically, is a quantity which may with the strictest accuracy be put into the Gibbs-Helmholtz equation for reversible isothermal processes.

It must now be emphasised that the decrease in the internal energy of the substances taking part in the reaction, that is, the calorimetrically measured heat of reaction, has nothing whatever to do with the *free energy* change accompanying the process, as measured by the electromotive force, except in so far as the two quantities are connected by the equation

$$A-U=\theta\frac{dA}{d\theta}$$

A and U for the Daniell cell happen to be nearly equal; this was for some time thought to demonstrate that the chemical energy, U, is always converted quantitatively into electrical energy. In the sense of the general equation, it merely means that $\frac{dA}{d\theta}$ is zero[*] in the Daniell cell, i.e. that the electromotive force does not vary with temperature. The temperature coefficient of the electromotive force may be either positive or negative. Therefore different cells may have A either greater than U or less than U. When A is less than U no difficulty arises; the excess of U over A appears as heat in the cell, which would warm if thermally insulated, and which gives out heat while working if maintained at constant temperature. When A is greater than U, heat has to be absorbed continuously from the surroundings while the cell is working; otherwise it would cool. The heat which is absorbed from the surroundings, together with the chemical energy, appear as work. The most striking example of a cell in which A and U differ very markedly is the concentration cell. In this cell two electrodes of the same metal dip into solutions containing an ionised salt of that metal at two different concentrations. The only 'chemical' process accompanying the working of the cell is the gradual equalisation of these concentrations, and if both are fairly small to begin with, there is no heat of dilution and thus $U=0$. But the electromotive force may be considerable—and depends upon the *ratio* of the two concentrations, however small they are absolutely Here we have a case in which A is supplied entirely from the heat of the surroundings

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[*] It would only obscure the argument to qualify the statement by reference to the Nernst Theorem at this point.

This state of affairs may at first sight appear strange, but we have seen that a perfect gas may perform work by expansion without change in internal energy, all the energy necessary for the expansion being derived from the heat of the surroundings This as we saw was easily interpreted in terms of the molecular theory, and constituted no departure from the second law The electrical energy yielded by a concentration cell is derived from the heat of the surroundings in an analogous way In some cases the electrical energy of a cell is derived from its chemical energy exclusively, and indeed the chemical energy may be more than sufficient to supply it In other cases there is a combination of the purely chemical process and the process typified by a concentration cell or the expansion of a gas The mechanisms of these more complicated cases are naturally more difficult to visualise than the simple case of the gas, but the physical interpretation will be developed further when we deal with the subject of entropy

FREE ENERGY AND SPONTANEOUS CHANGES

We have now to consider a point which is sometimes found a little confusing, namely, that the free energy change is under certain conditions a *measure of the tendency of a process to take place spontaneously*

To make matters clear we must first remember that there exists a certain definite permanent relation between given initial and final states of a system which is quite independent of any actual process by which the system passes from the one state to the other Let us take the concrete example of a gas at two different pressures P_1 and P_2, P_1 being greater than P_2 If the gas at pressure P_1 is given an opportunity of expanding isothermally so that its pressure falls to P_2 it will expand spontaneously The reverse change would not occur spontaneously. If the tendency to expand is opposed by a pressure P_2, then the gas at pressure P_1 will tend to expand, whilst that at the pressure P_2 will not The gas at the higher pressure thus has a greater expansive tendency

The work done in expansion to P_2 from P_1 depends, as we have seen, upon the way in which the expansion is allowed to take place It may vary from zero, when expansion is into a vacuum, up to a maximum of $R\theta \ ln \frac{P_1}{P_2}$ for a reversible expansion This maximum work, which we denote by A, has a single definite value It is primarily the actual work done by the gas during this definite process of expansion against an opposing pressure adjusted to the equilibrium value at each stage, and this is why we have so far regarded A as characteristic of the process itself

But now we might also regard this maximum work as a measure of the decreased tendency of the gas to expand We might think of the gas as possessing at pressure P_1 a certain capacity for performing work by expanding, and at pressure P_2 a diminished capacity The change in this capacity as the gas expanded from P_1 to P_2 would give the maximum work We thus define a difference between two states in terms of what would happen if the system passed reversibly from one to the other Even if the system passes irreversibly from the initial to the final state the change in the free energy is still the same If expansive tendency be a property of the gas having different values at pressures P_1 and P_2, then the change in this property must be the same however the transformation between the two states is brought about Even if the pressure of the gas falls without there being any performance of external work—expansion into a vacuum—the decrease in free energy is measured by the work which would have been done had the expansion been a reversible one

The change in free energy is in a sense analogous to a difference in potential, electric or gravitational The difference in gravitational potential between two points measures the work done in carrying unit mass from one to the other The maximum work obtainable from systems undergoing different kinds of change is therefore said to measure the decrease in a 'thermodynamic potential' of the systems There are several of these quantities we may consider the change to take place at constant temperature without any other restriction, or we may find it convenient to impose the condition of constancy of volume, or pressure Maximum work at constant pressure differs from that at constant volume, being greater by the term $p(v_2-v_1)$ as we have seen

There is however an important difference which makes the analogy with electrical or gravitational potential rather a superficial one The work done in conveying unit mass between two points is always equal to the change in gravitational potential, whatever be the path traversed, whilst, as we have just seen, the work performed by a system, such as the gas we have been considering, depends upon the 'path,' i e upon the nature of the stages intermediate between the initial and final ones Only when these intermediate stages are themselves equilibrium conditions is the work a definite maximum amount The maximum work, however, is an appropriate quantity by means of which to define the change in free energy or other 'thermodynamic potential' for another very important reason It is proved later in this chapter that *when a system can pass from a given initial state to a given final state by more than one reversible isothermal process then the maximum work performed is in each case the same* This is a principle of the greatest importance

To return to the gas expansion, let the gas be under a pressure P_1 and let the external pressure be P_0 The maximum work is $R\theta \ ln \frac{P_1}{P_0}$, and is greater the greater the value of P_1 So also is the tendency of the gas to expand spontaneously When $P_1=P_0$, that is the pressure of the gas is equal to the external pressure, $R\theta$ log $1=0$ The maximum work is zero, so also is the spontaneous expansion tendency. If P_1 becomes less than P_0 the value of the expression $R\theta \ ln \frac{P_1}{P_0}$ becomes negative, and this corresponds to the change from a tendency to expand to a tendency to contract

We see therefore in this very simple example that the maximum work is zero when there is no tendency for the system to pass from one state to another, and that it changes in sign when the direction of the spontaneous change is reversed

All this is of course quite obvious in the case of the gas expansion, and indeed the pressure itself would have done quite as well as the maximum work as a quantity in terms of which to define spontaneous expansion tendency But there are many natural changes, physical and chemical, in which the performance of work of expansion is merely a subsidiary process of insignificant importance, or one which at any rate can be allowed for in a ‘ correction term ’ The operation of cells, changes of crystalline form, chemical reactions are all capable of taking place not only at constant temperature but at constant volume Even when these processes take place at constant pressure the terms, $p(v_2-v_1)$, representing the work of expansion are usually small, and certainly quite insufficient to characterise the various transformations to which they belong

As many processes take place at constant pressure we will not neglect the term $p(v_2-v_1)$, but try first to indicate when it is of importance and when it is not If a gas expands till its pressure becomes equal to the external pressure it reaches a state of equilibrium and has no further tendency to expand But there may still exist tendencies for chemical changes to take place inside it If these take place there may be a further increase in volume But this new expansion is against an equilibrium pressure, it is reversible but has no fundamental connection with the chemical change The work we are really interested in therefore is $A-p(v_2-v_1)$, which we may call A' for the present

Only when we are interested in the *variation of the equilibrium pressure* p, as in the gas expansion, or in the cycle which gave us the influence of pressure upon melting point, do we consider $p(v_2-v_1)$ In this case A' is always zero Generally $\int p\,dv$ is the important term when we are dealing with variations in an equilibrium pressure, A' the important one when we are considering other variations in a system under an equilibrium pressure all the time

Let us consider the case of a super-cooled liquid, that is to say a liquid which has been cooled below the temperature at which it would be in equilibrium with solid, and which is therefore in an unstable condition It has a tendency to solidify spontaneously Solidification of a super-cooled liquid is an irreversible process, it represents the passage from a state where the system is not in equilibrium to one where the system is in equilibrium This is the only sort of modification which ever occurs spontaneously, and it is a quite general principle that all spontaneously occurring changes are irreversible because they all involve the passage into a state of equilibrium from an unstable state The only reversible processes that exist are, by definition, those in which the system passes through a series of adjacent states of equilibrium These processes are precisely the ones which have no tendency to take place of their own accord, although we frequently have occasion to imagine them to take place as a result of a continuous disturbance of the equilibrium to an infinitesimal extent

It is a general principle of great importance in thermodynamics that every spontaneously occurring process can be made to yield work, and this work is a maximum when the process is a reversible one It is not quite obvious, however, in every instance how this work toll is to be levied on the process Generally speaking, for every means we can devise for harnessing some spontaneously occurring process we can get a new thermodynamic result of some interest

The solidification of a super-cooled liquid ought to be capable of yielding work If a minute fragment of solid is dropped in to provoke crystallisation, there is certainly no work done except that due to the term $p(v_2-v_1)$, which may be positive or negative according as the volume of the solid is greater or smaller than that of the liquid We may suppose for simplicity that the specific volumes of solid and liquid are equal, in which circumstance the work done during this irreversible crystallisation is zero The problem is to devise a theoretical means by which the solidification can be made to take place in a reversible manner

In the present instance the solution of the problem is found by considering what must happen when the super-cooled liquid and the solid are placed respectively in the two arms of an inverted U-tube, hermetically sealed after all gas except the vapour of the substance has been pumped away Both solid and liquid tend to establish their saturated vapour pressure throughout the enclosure The vapour pressure of solid and of super-cooled liquid are not equal, the one with the greater vapour pressure yields a vapour which is supersaturated with respect to the other, and therefore must condense Thus a continuous process of distillation takes place until the form with the greater vapour pressure has passed over completely and condensed in the other form The form which increases must be the stable form, the solid in this instance It would be contrary to the nature of an unstable form to increase spontaneously at the expense of a stable form Thus the super cooled liquid has the greater vapour pressure The distillation process just indicated is irreversible, just as the direct solidification is irreversible, but it is now easy to see how the distillation may be carried out reversibly It is carried out in three stages, as follows

(i) At constant temperature θ, one gram molecule of the super-cooled liquid is allowed to vaporise under its own vapour pressure p_1 We thus obtain a volume V_1 of vapour, which is in equilibrium with the super-cooled liquid Work equal to $\int p dv = p_1 V_1$, since p_1 is constant, is done by the system

This vapour would not be in equilibrium with the solid, but would condense irreversibly upon it It would be in equilibrium with the solid if its pressure were reduced to p_2, the vapour pressure of the solid at θ

(ii) The vapour is isolated and allowed to expand till its pressure falls to p_2 This would happen spontaneously, but can be controlled and made to yield the maximum work in a reversible expansion If the vapour obeys Boyle's law this work is $R\theta\, ln\frac{p_1}{p_2}$

Let the new volume of the vapour be V_2

(iii) This vapour is now placed in contact with the solid It is in equilibrium, but may be reversibly condensed by an infinitesimal increase in the external pressure on a piston confining the vapour over the solid Reversible work equal to $p_2 V_2$ is done on the system during the condensation

The super-cooled liquid has now been transformed by a completely reversible process into the solid The total work done by the system is given by

$$p_1 V_1 + R\theta\, ln\frac{p_1}{p_2} - p_2 V_2$$

The vapour is assumed to behave in accordance with Boyle's law, therefore we have approximately $p_1 V_1 = p_2 V_2$ And the work is therefore,

$$R\theta\, ln\frac{p_1}{p_2}.$$

A certain approximation was made in the above calculation, which should be pointed out but is unimportant The work done in the reversible vaporisation was taken as $p_1 V_1$, and in the condensation as $p_2 V_2$ Quite accurately these terms should be $p_1(V_1 - v_1)$ and $p_2(V_2 - v_2)$ where v_1 and v_2 are the volumes of the liquid and solid respectively. This would lead to a final expression $R\theta\, ln\frac{p_1}{p_2} + (p_2 v_2 - p_1 v_1)$ The last term is very small, but that by itself is not the reason we are unconcerned with it It comes from the *reversible* processes in stages (i) and (iii) The only process which measured the tendency of the liquid to solidify was the process in (ii), namely, the expansion of the vapour from *the state where it was in equilibrium with the super-cooled liquid to the state where it was in equilibrium with solid* The maximum work obtainable from this one spontaneous process is the work with which we are concerned—even if the approximation did not make it the only term in the final result

The term $R\theta\, ln\frac{p_1}{p_2}$, representing the maximum work obtainable from the process of solidification, can be regarded as a measure of some difference between the super-cooled liquid and the solid, which is independent of any actual way in which solidification takes place $R\theta\, ln\frac{p_1}{p_2}$ is the difference between the free energy of the vapour at pressure p_1 and its free energy at pressure p_2 We have thus measured the tendency of the liquid to solidify in terms of the difference in free energy of the vapour in equilibrium with liquid and solid respectively

At the melting point of the liquid $p_1 = p_2$, and thus the tendency to solidify is zero

Since p_1 and p_2 vary continuously with temperature, and since below the melting point $p_1 > p_2$ whilst at the melting point $p_1 = p_2$, above the melting point p_2 must be greater than p_1 Thus, if the superheated solid could exist, it would have a greater vapour pressure than the liquid at the same temperature The tendency of the liquid to freeze would be $R\theta\, ln\frac{p_1}{p_2}$, which is a negative quantity Thus the tendency to solidify has become negative, that is, it has changed into a tendency for solid to melt The sign of the work term indicates the direction in which the process tends to take place

We now turn to the proof of a principle already enunciated It is frequently possible to devise more than one isothermal reversible process by means of which a system can be brought from a given initial condition to a given final condition By a direct application of the second law of thermodynamics it can be shown that the work done by the system in each of the reversible processes is the same in amount

Let us suppose that there are two such processes, which we will refer to as process 1 and process 2 Let the work done by the system when it undergoes process 1 be A_1, and that done when it undergoes process 2 be A_2 Let the system pass from its initial to its final state by process 1 A_1 is performed at constant temperature θ Now let the system return to its initial state once more by process 2 Since A_2 would have been done by the system had it passed from the initial to the final state by process 2, the reverse change necessitates the performance of work A_2 on the system

The system has completed a cycle of changes at constant temperature It is back in its initial state, therefore no work can have been performed at the expense of its internal energy Moreover, its volume and pressure are unchanged Hence, no net work has been done on it by the external pressure The net work performed by the system during the cycle is A_1-A_2 This could only have been done at the expense of the heat of the surroundings This is in direct contradiction to the experience summarised in the second law of thermodynamics, for the whole cycle has been carried out at constant temperature If the second process had been carried out at a lower temperature, then the first A_1-A_2 might have had a positive value, as in Carnot's cycle, because there could have been a 'compensating' passage of heat from a reservoir at a higher temperature to one at a lower temperature This in the present instance is ruled out by the isothermal nature of the cycle Thus, no work can have been performed as a net result of the cycle Therefore $A_1-A_2=0$, or $A_1=A_2$

Thus every process which can be devised must have the same value of A This fact renders the value of A independent of the specific mechanism of the device, and incidentally justifies the employment of A as a measure of the difference between two states of a system.

We may state the result in the form that the net work done in an isothermal reversible cycle is zero This is a principle of great importance in thermodynamical calculations. It is necessary to guard against the error of supposing it to be a consequence of the conservation of energy in any way It is a direct consequence of the second law The first law would not contradict the possibility that work might have been done at the expense of heat absorbed

CHANGE OF STATE

We may now illustrate this principle, and at the same time show how there may be several reversible means of transforming a system, by considering the transformation of one allotropic form of a metal into another. We may take the oft-quoted example of the interconversion of grey and white tin. Above the transition point the white form is stable, below the transition point it tends to pass spontaneously into the grey form. At the transition point the two forms are in equilibrium, and the transformation from one into the other in the solid state is reversible. No work is then done except that depending on the difference in specific volumes, $p(v_2-v_1)$. At any other temperature, θ, the transformation from the unstable form to the stable form is an irreversible change, analogous to the freezing of a super-cooled liquid.

By a process of distillation, exactly analogous to that by which the reversible conversion from super-cooled liquid to solid was effected, we can conduct the whole change in a strictly reversible manner. We find that the work done by the system when a gram molecule of white tin is transformed reversibly into grey tin is

$$R\theta \ln \frac{p_{white}}{p_{grey}},$$

p_{white} and p_{grey} being the respective vapour pressures.

We have, as before, and for the same reason, omitted the factor depending on the different specific volumes and the external pressure. The expression represents the decrease in free energy when white tin under its own vapour pressure changes into grey tin under its vapour pressure.

The conversion can be brought about reversibly in another way. A galvanic cell is made in which the electrodes are respectively of white and grey tin, and the electrolyte is a solution of a salt of tin. At temperatures where grey tin is the stable form the cell possesses an electromotive force such that when current flows grey tin is deposited on the grey tin electrode and white tin dissolves. The work which would be performed during the reversible conversion of a gram molecule is nEF, where n is the valency of the tin ions in solution, and E is the electromotive force of the cell. At the transition temperature there is no tendency for either form to increase at the expense of the other, and the electromotive force becomes zero, whilst above the transition point it changes sign, the current now tending to flow in such a direction that the grey tin electrode dissolves and the white tin electrode grows at its expense

At any temperature the work done in these two alternative conversion processes is the same

$$nEF=R\theta\, ln\frac{p_{white}}{p_{grey}},$$

the appropriate units of work being used

Yet another method by which allotropic forms of a substance may be interconverted isothermally and reversibly will be described when we have touched upon the theory of solution, which we may now proceed to do

SOLUTIONS

Once more the general principle stands out that if a system tends to change spontaneously it cannot be in equilibrium, and if it is not in equilibrium, then a resultant force of some kind can be found, if the resultant force is unopposed no work is performed, while if a means of opposing it is found, then the whole change can be made to yield work The amount of work increases with the magnitude of the opposing force and has its greatest value when the opposing force is just equal to the driving force The change now takes place in a reversible manner, through a series of states of equilibrium

As we have already pointed out, the application of these ideas is very obvious in such simple mechanical systems as the expansion of a gas, or the movement of a particle under the action of mechanical forces But in dealing with physical and chemical changes in general the problem is to conduct any particular transformation in such a way that a resultant force reveals itself, and thus presents something to which mechanical opposition may be offered In the case of the gas expansion the resultant force is simply the difference between the pressure of the gas and the external pressure In the case of the super-cooled liquid the matter is more obscure, but, as we have seen, the resultant force can be found in the difference between the vapour pressures of liquid and solid In the theory of solution the osmotic pressure plays the decisive part

One of the most fundamental facts about a solution is that the dissolved substance tends to diffuse spontaneously from the more concentrated parts to the less concentrated parts of the solution until equality of concentration is established throughout This is an obvious consequence of the molecular nature of matter, for the molecules of the solute move about continually among the molecules of solvent until on the average there are equal numbers of solute molecules in each unit volume of solution The equalisation of concentration by diffusion, as we ordinarily perceive it, is an irreversible process A solution of uniform concentration does not separate again into a more concentrated and a less concentrated portion Yet, following the general trend of the ideas in this chapter, we should infer from the fact that diffusion occurs spontaneously a difference of free energy between concentrated and dilute solution This should be capable of manifesting itself as external work if the equalisation of concentrations could be conducted reversibly

The device known as a semi-permeable membrane, of which practical use is made in the measurement of osmotic pressure, enables this to be done By its aid it is possible to bring a solution reversibly from any concentration to any other

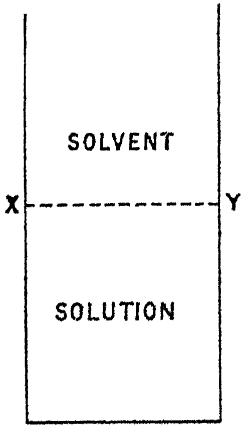

FIG 4

We imagine a vessel in which solution and solvent are separated, as in the figure, by a movable piston XY, the piston being a semi-permeable membrane, i e. one which allows solvent to pass through freely but not solute Then it is an experimental fact that a pressure will be exerted on the membrane tending to drive it upwards Since it is freely permeable to the solvent it moves unimpeded, while the solvent streams through it into the solution which thus becomes diluted By the application of mechanical pressure to the piston its movement may be stopped The mechanical pressure which needs to be applied to prevent the movement, and thus to prevent the entry of solvent into the solution, is said to be equal to the osmotic pressure of the solution

If the piston is allowed to move outward unopposed under the influence of the osmotic pressure no work is performed But if it is allowed to move outward against an opposing pressure differing by an infinitesimal amount only from the osmotic pressure π, then the work done is $\pi a dx$, where a is the area of the piston and dx the distance through which it moves This equals πdV where dV is the volume of solvent which has entered the solution If the process is allowed to proceed so that the volume of the solution increases from V_1 to V_2, then the work done is

$$\int_{V_1}^{V_2} \pi dV$$

In this integral π is not constant but depends upon the dilution To evaluate the work the relation between π and V must be known

The dilution from volume V_1 to volume V_2 is exactly equivalent to the diffusion of the dissolved substance from a volume V_1 of solution into an additional volume (V_2-V_1) of pure solvent

We may say that the decrease in free energy of the solution during the process of dilution from volume V_1 to V_2 is given by

$$A=\int_{V_1}^{V_2} \pi dV$$

It will be noticed that a simplifying assumption has been made, namely, that solvent and solution may be mixed without appreciable contraction or expansion This is very nearly true unless the solution is very concentrated to begin with

The existence of an osmotic pressure in the above sense being an experimentally established fact, it is quite justifiable to use it in calculations of free energy changes without further enquiry into its nature Strongly expressed but quite unfounded objections have sometimes been raised against the use of the osmotic pressure in thermodynamical calculations But inspection of the alternative methods always reveals that they involve the tacit assumption of just those properties of the solution which are most simply expressed in terms of the osmotic pressure

The application of the Gibbs-Helmholtz equation leads at once to an interesting result, namely, that under certain conditions the osmotic pressure must be directly proportional to the absolute temperature

Let the process to which the equation is applied be the reversible passage of a volume dV of solvent into the solution, there being no total volume change

$$A-U=\theta\frac{\partial A}{\partial\theta}$$

$$A=\pi dV$$

The change in internal energy of the solution is equal to the heat which would be evolved if the dilution took place in a calorimeter without the performance of work If l be the heat evolved when unit volume of solvent is poured into the solution, then the heat evolved when dV is added is ldV This is equal to U We have, therefore,

$$\pi dV-ldV=\theta\frac{\partial(\pi dV)}{\partial\theta},$$

$$\pi dV-ldV=\theta\frac{\partial\pi}{\partial\theta}dV,$$

dV being an arbitrarily chosen quantity, we may treat it as constant during the differentiation with respect to temperature Moreover, although the semi-permeable membrane sweeps out a volume dV within the confines of the system, the *total* volume is assumed to remain constant We are thus dealing with A_v and $\left(\frac{\partial A}{\partial\theta}\right)_v$

In the case where the volume of the solution is already fairly dilute the heat of dilution will be small If it can be neglected we shall have

$$\pi dV=\theta\frac{\partial\pi}{\partial\theta}dV,$$

$$\frac{d\pi}{\pi}=\frac{d\theta}{\theta},$$

$$ln\ \pi=ln\ \theta+\text{constant},$$

$$\pi=\text{constant}\ \theta.$$

CHEMICAL REACTIONS

We have now considered free energy changes associated with the expansion of gases, changes of state or allotropic condition, the working of galvanic cells, and the diffusion of dissolved substances It remains to consider another great class of spontaneously occurring natural processes, namely, chemical reactions The case of reactions between solid substances is almost exactly analogous to the interconversion of allotropic forms and may be treated in a similar way We may therefore proceed to the case of reactions between gases

The chemically reversible reaction $CO+H_2O \rightleftharpoons CO_2+H_2$ will serve as an example

The system of gases will be supposed to be at constant temperature, and for the sake of simplicity, at such a temperature that the reactions proceed rapidly to equilibrium. A mixture of carbon monoxide and steam in equivalent proportions reacts to form carbon dioxide and hydrogen until the proportions of all four gases have obtained definite equilibrium values The same equilibrium is reached when an equimolecular mixture of carbon dioxide and hydrogen is the starting point Any mixture of the four gases changes spontaneously until an equilibrium point is reached When pure carbon monoxide and steam react to give an equilibrium mixture there is a decrease in free energy , when pure carbon dioxide and hydrogen react there is likewise a decrease in free energy On whichever side of the equilibrium a given mixture of gases happens to be, it tends to change into the equilibrium mixture with a decrease in free energy

These changes are irreversible , moreover, if the reaction takes place at constant volume no work is done (It is necessary to guard against any confusion between the reversibility of the reaction in the chemical sense, which only means that equilibrium can be reached from either side, and thermodynamic reversibility The irreversibility of the changes we are considering consists in the fact that when the system passes from either side to equilibrium it cannot change back again out of the equilibrium state The equilibrium mixture cannot change spontaneously into pure carbon dioxide and hydrogen, or into pure carbon monoxide and steam) As no work is done the change in the internal energy of the substances taking part in the reaction will appear as heat—the heat of reaction This will be in the form of heat evolved when equilibrium is reached from one side, heat absorbed when it is approached from the other side In the reaction we have chosen for an example,

$$CO+H_2O=CO_2+H_2+10{,}000 \text{ cals}$$

Thus, when any carbon dioxide and hydrogen are formed at the expense of carbon monoxide and water, heat is given out, that is, the internal energy of the system decreases, and vice versa

It is at once obvious that the attempt to measure the tendency of the reaction to take place spontaneously by the heat evolved is hopeless, since the reaction will go spontaneously with either absorption or evolution of heat according to the relation of the initial proportions of the gases to the equilibrium proportions This objection does not in the least apply to the measurement of the tendency by the decrease in free energy

A device for carrying out such chemical changes in a reversible manner was thought out by van't Hoff, and goes by the name of the 'equilibrium box'

The equilibrium box is a closed vessel which contains in its sides a number of windows of different materials permeable respectively to each separate component of the gaseous reaction mixture and to none of the others It does not matter whether such a contrivance is realisable in practice, although as a matter of fact a vessel made of palladium is completely permeable to hydrogen at high temperatures, and not to any other gas, so that the principle of the equilibrium box is accurately realised in this one instance at least

We have now to imagine carried out a slightly cumbrous

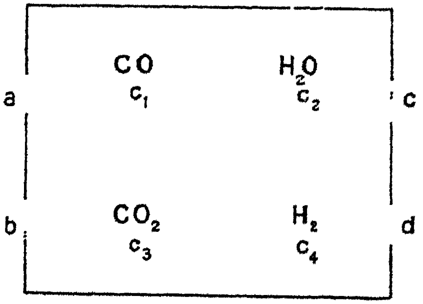

FIG 5

process whereby a given mixture of carbon monoxide and steam may be converted reversibly into carbon dioxide and hydrogen The figure shows the equilibrium box, in which *a*, *b*, *c*, and *d* are respectively permeable only to carbon monoxide, to steam, to carbon dioxide, and to hydrogen Let the enclosure contain a mixture of all the gases in equilibrium, the concentrations being c_1, c_2, c_3, and c_4 respectively

We are supposed to be given a gram molecule of carbon monoxide at the concentration C_1, and a gram molecule of steam at C_2, these being quite arbitrarily chosen concentrations * It is required to find the amount of work which can be obtained when these are converted reversibly into carbon dioxide and hydrogen at the concentrations C_3 and C_4 respectively, these, likewise, being arbitrarily chosen

The carbon monoxide and the steam are respectively compressed or allowed to expand until their concentrations

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* We suppose the gases not to be mixed at the start This, however, is not essential to the proof as gases in a mixture at concentrations C_1 and C_2 can be separated reversibly and without the expenditure (or gain) of any work The method is as follows, the idea being due to Planck

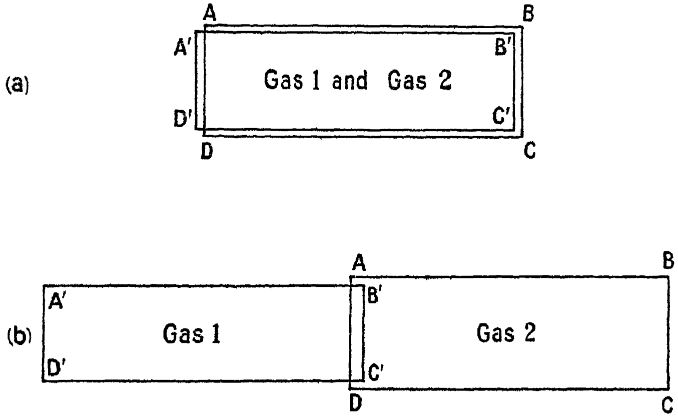

FIG 6

ABCD makes a gas-tight fit over *A'B'C'D'*, and may be moved in and out There are gas-tight joints which permit this

B'C' is permeable to gas 2 but not to gas 1

AD is permeable to gas 1 but not to gas 2

By pulling out from position (a) to position (b) the gases are separated reversibly and without expenditure of work, the final concentration of each separate gas being equal to its concentration in the original mixture alter to the corresponding equilibrium box values, c_1 and c_2 If the volumes have to change from V_1 to v_1 and from V_2 to v_2, the work done in the two cases is $R\theta\, ln\frac{v_1}{V_1}$ and $R\theta\, ln\frac{v_2}{V_2}$, and, since concentration is inversely proportional to volume, we have $A_1=R\theta\, ln\frac{C_1}{c_1}$ and $A_2=R\theta\, ln\frac{C_2}{c_2}$

We have now brought reversibly one gram molecule of each from the given initial state to the concentration prevailing in the equilibrium box Each can now be placed in contact with its appropriate window *a* or *b*, without any irreversible diffusion taking place, and can then be slowly introduced into the equilibrium box through its semi-permeable membrane Inside the box reaction is supposed to take place rapidly As the carbon monoxide and steam react equivalent amounts of carbon dioxide and hydrogen are formed and are continuously removed through *c* and *d* respectively at the concentrations c_3 and c_4 During the whole process the state of affairs inside the equilibrium box remains unchanged No work is done during the process, since that required to push the carbon monoxide and steam reversibly into the enclosure is exactly balanced by that which is performed when the carbon dioxide and hydrogen are removed

The concentrations of the carbon dioxide and of the hydrogen are now respectively altered from c_3 and c_4 to C_3 and C_4, whereby the work done by the gases is given thus *

$$A_3=R\theta\, ln\frac{c_3}{C_3} \text{ and } A_4=R\theta\, ln\frac{c_4}{C_4}$$

The total work in the whole process is $A_1+A_2+A_3+A_4$, thus

$$A=R\theta\left\{ln\frac{C_1}{c_1}+ln\frac{C_2}{c_2}+ln\frac{c_3}{C_3}+ln\frac{c_4}{C_4}\right\},$$

or

$$A=R\theta\left\{ln\frac{C_1C_2}{C_3C_4}-ln\frac{c_1c_2}{c_3c_4}\right\}$$

It will be noted that if C_1, C_2, C_3, C_4 are equal to the equilibrium concentrations, $A=0$

Again, if we start with concentrations of carbon monoxide and hydrogen greater than the equilibrium concentrations, i e $C_1>c_1$ and $C_2>c_2$, and finish with carbon dioxide and hydrogen at the equilibrium concentrations, i e $C_3=c_3$, and $C_4=c_4$, A is positive, whilst if $C_1<c_1$ and $C_2<c_2$, A is negative

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* The terms $R\theta\, ln\frac{c_3}{C_3}$ and $R\theta\, ln\frac{c_4}{C_4}$ have the equilibrium concentrations in the numerator, since we are calculating the work done *by* the system in each case This is only positive if c_3 is greater than C_3, etc.

We shall have occasion to return to the above equation later in dealing with the law of mass action, which follows almost immediately from it

SUMMARY

To summarise the results of the present chapter—all spontaneously occurring processes may be made to yield work if conducted reversibly The work performed by a system changing at constant temperature from a given initial state to a given final state by several alternative processes has a maximum value for a reversible process, and the same value for all reversible processes This constant maximum value is equal to the decrease in free energy of the system (by definition)

It is for many purposes convenient to separate the net work done against the external pressure as a result of any volume changes from the remainder of the work The difference made by subtracting the work of expansion is usually small Two phases of a substance may be in equilibrium under an external pressure , when the phase of smaller specific volume passes into the phase of larger specific volume, reversible work to the extent of $p(v_2-v_1)$ is done, but any other work must be zero at the equilibrium temperature

The total work performed by a system which has undergone a cycle of reversible changes at constant temperature is zero

By conducting a reversible process at the temperature θ, and reversing at $\theta-d\theta$, a relation between the maximum work at constant volume A_v and the change in internal energy of the system is found

$$A_v-U=\theta\left(\frac{\partial A_v}{\partial\theta}\right)_v$$

An analogous equation may be found for changes taking place subject to conditions other than constancy of volume

The calculation of A in the case of change of state depends upon the difference in the vapour pressures of the two forms, in the case of solutions upon the existence of the osmotic pressure, and in the case of chemical reactions between gases upon the use of the van't Hoff equilibrium box

CHAPTER V

APPLICATIONS OF THE ISOTHERMAL REVERSIBLE CYCLE

FROM the discussion of the previous chapter the principle emerged that the net work done by a system traversing an isothermal reversible cycle is zero An exactly equivalent statement is that if a system can pass from an initial to a final state at constant temperature by two or more reversible processes, then the amount of work done is the same in each case This is at once seen to be true by imagining the system to change from the initial to the final state by one process, and then to be brought back again to its initial state by the second process, when the net work performed is zero A third way of stating the principle is to say that the decrease in free energy attending the passage of a system from one state to another is a characteristic quantity independent of the particular reversible path chosen for the purpose of evaluating the free energy change

A few applications have already been considered in illustration of the principle In this chapter further applications will be given for their intrinsic importance, and to illustrate various methods of attack on specific problems

THE THEORY OF SOLUTIONS

Van't Hoff showed how the tendency of a solute to diffuse could be made the basis of a thermodynamical theory of solutions The free energy changes accompanying the dilution of a solution are calculated in terms of the osmotic pressure

We shall follow van't Hoff's method, despite the objection which has sometimes been raised that the osmotic pressure is not a property of fundamental importance This objection seems to be without any validity at all The second law of thermodynamics can be regarded as a direct consequence of the molecular-kinetic nature of matter This molecular-kinetic nature shows itself in its most primitive form in the tendency of a solute to diffuse in solution The osmotic pressure is the direct measure of this tendency Thus, from the theoretical point of view the osmotic pressure is the most fundamental property of the solution That its practical measurement is difficult is irrelevant Thermodynamics introduces it only in the intermediate stages of the derivations, it does not necessarily enter into the final results

We have seen that when a solution is diluted reversibly by the movement of a semi-permeable membrane so that a volume dV of solvent enters the work performed by the system is πdV, where π is the osmotic pressure Conversely, to concentrate the solution by pushing in the piston so that a volume dV of solvent leaves the solution, the osmotic work πdV has to be performed on the system

LOWERING OF VAPOUR PRESSURE

Every solution of a non-volatile solute has a lower vapour pressure than the pure solvent If the solute is itself volatile the total vapour pressure of the solution may be greater or less than that of the solvent, but the partial pressure of the solvent in the vapour over the solution is always less than the vapour pressure of the pure solvent It is clear on general grounds that this lowering of vapour pressure by a dissolved substance is intimately connected with the existence of an osmotic pressure For the existence of an osmotic pressure means that work must be done in concentrating the solution When a solution loses solvent by evaporation it becomes more concentrated This involves the performance of osmotic work On the other hand, osmotic work does not have to be performed in this way when the vapour leaves the pure solvent Hence, the solution has less tendency to vaporise than the solvent, and possesses a lower vapour pressure

This difference in vapour pressure between solvent and solution may be made the basis of a process for carrying out the dilution of the solution in a reversible manner, just as the analogous difference in vapour pressure between solid and super-cooled liquid was utilised for the calculation of the free energy in the example discussed in the last chapter

The operation is conducted in the following three stages For simplicity it is assumed that the solvent only is volatile

(1) dn gram molecules of solvent vapour are allowed to vaporise under the actual vapour pressure p_0 of the solvent

Work performed by the system $=p_0v_0$

(ii) If this vapour were placed in contact with the solution it would condense irreversibly, because its pressure is greater by a finite amount than the vapour pressure of the solution In order that it may be condensed reversibly into the solution it must first be allowed to expand isothermally until its pressure falls to a value p, at which it is in equilibrium with the solution This is the new vapour pressure

The work performed in this expansion is $dnR\theta\, ln\frac{p_0}{p}$ (i e $R\theta\, ln\frac{p_0}{p}$ per gram molecule) if the vapour obeys Boyle's law

(iii) The volume of the vapour is now v A pressure p is now applied and the whole is condensed into the solution

Work performed on the system $=pv$

Using once more the assumption that the vapour obeys Boyle's law, we see that this term pv cancels the term p_0v_0 of the first operation

We are thus left with

$$dnR\theta\, ln\frac{p_0}{p}$$

as the decrease in free energy attending the dilution of the solution with dn gram molecules of solvent

RELATION OF OSMOTIC PRESSURE TO LOWERING OF VAPOUR PRESSURE

Decrease in free energy of solution when diluted with volume dV of solvent, calculated osmotically

$$=\pi dV$$

Decrease in free energy of solution when diluted with dn gram molecules of solvent, calculated from vapour pressures

$$=dnR\theta\, ln\frac{p_0}{p}.$$

Provided that dV be chosen so as to be the volume of liquid solvent which gives dn gram molecules of solvent vapour, these two expressions must be equal

$$\pi dV=dnR\theta\, ln\frac{p_0}{p},$$

$$\pi=\frac{dn}{dV}R\theta\, ln\frac{p_0}{p}$$

$\frac{dn}{dV}$ may be transformed as follows dn gram molecules of solvent vapour$=M_0 dn$ grams, where M_0 is the molecular weight of the solvent *as vapour*

This mass of solvent occupies a volume dV litres or $1000dV$ c cs as liquid

Hence $\frac{M_0 dn}{1000dV}=\rho$, where ρ is the density of the solvent in grams per c c

Therefore
$$\frac{dn}{dV}=\frac{1000\rho}{M_0},$$
$$\pi=\frac{1000\rho}{M_0}R\theta\, ln\frac{p_0}{p}$$

This relation between the osmotic pressure of the solution and the vapour pressures of solvent and solution holds good only when the vapour of the solvent behaves in accordance with Boyle's law When the vapour pressure is not very large this assumption is not far from the truth M_0, it should be remembered, is the molecular weight of the solvent in the vapour state This is important because the molecular weight in the vapour state usually has the simple value indicated by the chemical formula, while the actual molecular complexity of the solvent in the liquid state is often a matter of considerable doubt

As an example of the use of the above equation we may calculate indirectly the osmotic pressure of a certain benzene solution of a non-volatile substance, the vapour pressure at 30° C is found to be 110 1 mm, while that of pure benzene at the same temperature is 120 3 mm

In deriving the formula we measured the volumes in litres, it will be convenient to calculate the osmotic pressure in atmospheres R must therefore be measured in litre-atmospheres, in which units its value is 0 0821

ρ=density of benzene at 30°=0 83,
M_0=molecular weight of benzene vapour=78,
$\theta=273+30=303$.

$$\text{Therefore } \pi=\frac{1000\times 0\ 83\times 0{\cdot}0821\times 303}{78}\ ln\frac{120\ 3}{110\ 1}.$$

$$\pi=\left(\frac{1000\times 0\ 83\times 0\ 0821\times 303}{78}\right)\times 2\ 303\ \log_{10}\frac{120\ 3}{110{\cdot}1}\text{ atmospheres}$$

If p_0 and p are not very widely different, $ln\frac{p_0}{p}$ is approximately equal to $\frac{p_0-p}{p}$ The simplified form is often used

We then have $$\frac{p_0-p}{p} = \frac{M_0\pi}{1000\rho R\theta}$$

CONSEQUENCES OF THE VAPOUR PRESSURE LOWERING ELEVATION OF BOILING POINT AND DEPRESSION OF FREEZING POINT

The well known elevation of the boiling point and depression of the freezing point of a solvent by a dissolved substance are direct consequences of the lowering of the vapour pressure They are thus related to the osmotic pressure We have seen that the existence of osmotic pressure makes it necessary that work should be done when a solution is concentrated. The consequence is that vapour leaves the solution less readily than it leaves the pure solvent Loss of solvent either by boiling off or by freezing out tends likewise to concentrate a solution Hence a solution freezes and boils less readily than a pure liquid In other words, the boiling point is higher and the freezing point lower

ELEVATION OF BOILING POINT

Small elevations of boiling point may be calculated as follows

At the boiling point θ of the pure solvent its vapour pressure p_0 is equal to the external pressure

At θ the vapour pressure p of the solution is less than that of the pure solvent by an amount $p_0 - p = \Delta p$

To cause the solution to boil either the external pressure must be lowered or else the temperature must be raised by an amount $\Delta\theta$ sufficient to increase the vapour pressure by Δp, and thus make it equal to the external pressure

For small differences $\frac{\Delta p}{\Delta\theta} = \frac{dp}{d\theta}$, where $\frac{dp}{d\theta}$ is the rate of

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$$* \frac{p_0}{p} = 1 + \frac{p_0-p}{p},$$

$$ln\frac{p_0}{p} = ln\left(1 + \frac{p_0-p}{p}\right),$$

$$= \frac{p_0-p}{p} - \tfrac{1}{2}\left(\frac{p_0-p}{p}\right)^2 \ldots\ldots$$

Since $ln(1+x) = x - \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 \ldots$

change of the vapour pressure of the solution with temperature in the neighbourhood of θ

At the beginning of Chapter IV we found for the variation with temperature of the saturated vapour pressure

$$\frac{dp}{d\theta}=\frac{l}{\theta(v_2-v_1)}$$

This may be simplified by neglecting v_1 the specific volume of the liquid in comparison with v_2 that of the vapour, and multiplying top and bottom by the molecular weight of the vapour, we then have

$$\frac{\Delta p}{\Delta\theta}=\frac{L}{\theta V},$$

where L is the molecular latent heat of the solvent, which for dilute solutions we may take as equal to that of the solution, and V is the molecular volume of the solvent vapour If the solvent vapour obeys Boyle's law $p\,V=R\theta$, and, substituting for V, we obtain

$$\frac{\Delta p}{\Delta\theta}=\frac{L}{\dfrac{R\theta^2}{p_0}},$$

$$\frac{1}{p_0}\Delta p=\frac{\Delta\theta\, L}{R\theta^2},$$

$$\frac{p_0-p}{p_0}=\frac{\Delta\theta\, L}{R\theta^2}$$

But from the relation between osmotic pressure and lowering of vapour pressure we have approximately

$$\frac{p_0-p}{p_0}=\frac{M_0\pi}{1000\rho R\theta}$$

Since p_0 and p do not differ very much

Therefore $$\frac{\Delta\theta\, L}{R\theta^2}=\frac{M_0\pi}{1000\rho R\theta},$$

$$\Delta\theta=\frac{M_0\pi\,\theta}{1000\rho\, L}=\frac{\pi\theta}{1000\rho\, l},$$

where l is the latent heat of vaporisation per *gram* of solvent

This gives the elevation of boiling point in terms of the osmotic pressure

The formula is only approximate, and applies only to small elevations The assumptions made which limit its generality are

(i) That the elevation is sufficiently small to justify the use of the approximation $\frac{\Delta p}{\Delta \theta} = \frac{dp}{d\theta}$ at θ

(ii) That the solution is sufficiently dilute to possess a latent heat of vaporisation practically equal to that of the solvent—or more strictly that the ratio of the two latent heats is not far from unity

(iii) That the vapour of the solvent behaves in accordance with Boyle's law.

DEPRESSION OF FREEZING POINT

This may be calculated in an analogous manner to the elevation of boiling point It is assumed that solute does not freeze out with the solvent in the form of mixed crystals At the freezing point of the solvent the vapour pressures of liquid and solid solvent are equal Otherwise they could not remain in equilibrium At this temperature the vapour pressure of the solution is lower than that of the pure liquid solvent, and, therefore, than that of the solid At some temperature, however, a point may be found at which solid solvent and solution have the same vapour pressure This will be the freezing point of the solution, because at this temperature there is no tendency for vapour to distil either

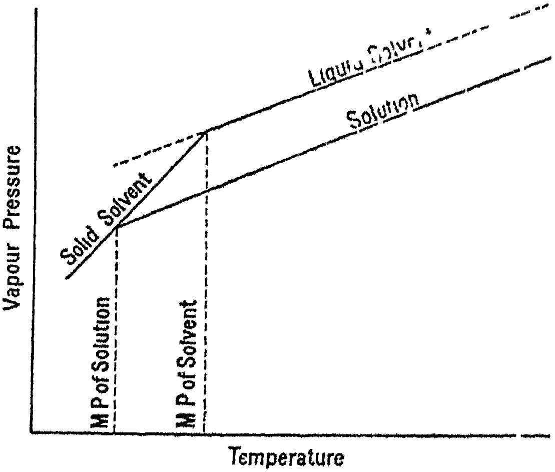

FIG 7

from solid to solution, or vice versa, so that the two are in equilibrium That the freezing point of the solution must be lower than that of the solvent is easily seen from the relative position of the three vapour pressure curves in the figure The vapour pressure curve of the liquid solvent must be less steep than that of the solid, because the liquid curve produced must lie above the solid curve This is shown by the dotted curve, and merely represents the familiar fact that the super-cooled liquid must have the higher vapour pressure

Let $p_0 - p = \Delta p$ be the difference in vapour pressure between the liquid or solid solvent and the solution at θ, the freezing point of the solvent

We have to find a temperature decrease $\Delta\theta$ such that the corresponding difference in vapour pressure between solid and solution falls from Δp to zero The vapour pressure of the solid falls with temperature according to the equation $\frac{dp_s}{d\theta} = \frac{L_s}{\theta V}$, while that of the solution falls at the rate $\frac{dp_l}{d\theta} = \frac{L_l}{\theta V}$, where L_s and L_l are the molecular latent heats of vaporisation of solid and liquid (the latter taken as equal to that of the solution) and V is the volume occupied by a gram molecule of the vapour It is to be noted that since L_s is greater than L_l, the vapour pressure of the solid falls more rapidly than that of the solution Thus, although greater to begin with, it will presently become equal to that of the solution The *relative* rate of change of vapour pressure of solid and solution will be

$$\frac{d(p_s - p_l)}{d\theta} = \frac{dp_s}{d\theta} - \frac{dp_l}{d\theta} = \frac{L_s - L_l}{\theta V},$$
$$= \frac{L}{\theta V},$$

where L is the molecular latent heat of *fusion*, since from the first law, heat of vaporisation of solid − heat of vaporisation of liquid = heat of fusion of solid

The relative change in vapour pressure required is Δp, so that

$$\frac{\Delta p}{\Delta\theta} = \frac{L}{\theta V}$$

From this we find in exactly the same manner as in the last section

$$\Delta\theta = \frac{\pi\theta}{1000\rho l},$$

with the difference that l is now the latent heat of fusion instead of the latent heat of vaporisation of the solvent

THE RELATION BETWEEN OSMOTIC PRESSURE AND CONCENTRATION

In order to make further use of the equations which have just been found, it is necessary to know the relation between the osmotic pressure of a solution and its concentration To arrive at this knowledge we require considerations of a more specific nature than those based purely upon the second law of thermodynamics Given the existence of the osmotic pressure the second law is sufficient to establish the necessary connection between this and the various phenomena associated with lowering of vapour pressure To go a step further and connect the osmotic pressure with the concentration of the solution, we need a molecular theory of osmotic pressure. For the purposes of thermodynamics, a purely empirical relationship, based upon the result of experiment, is equally useful

Van't Hoff showed that in the case of sufficiently dilute solutions the osmotic pressure is equal to the pressure which the solute would exert if it occupied the same volume in the state of gas A law analogous to Boyle's law applies to dilute solutions, thus the osmotic pressure can be calculated from the equation $\pi V = R\theta$ where π is the osmotic pressure, and the concentration of the solution is such that 1 gram molecule of solute occupies V litres R has the same value as in the gas equation. If the concentration of the solution be c gram molecules per litre, $c = \frac{1}{V}$, and thus $\pi = cR\theta$ Experiment confirms this relation in the case of dilute solutions

DILUTE SOLUTIONS

For the lowering of vapour pressure we have found the result $\pi = \frac{1000\rho}{M_0} R\theta \ln\frac{p_0}{p}$. Introducing the van't Hoff value for the osmotic pressure, this becomes

$$cR\theta = \frac{1000\rho}{M_0} R\theta \ln\frac{p_0}{p} \quad \text{or} \quad \ln\frac{p_0}{p} = \frac{cM_0}{1000\rho}.$$

This may be put in a still simpler form c is the number of gram molecules of solute in a litre of solution

1000ρ=total mass of solvent in a litre of solvent.
=total mass of solvent in a litre of solution approximately

Therefore $\frac{1000\rho}{M_0}$=number of gram molecules in a litre

Therefore $\frac{cM_0}{1000\rho}$ may be written as $\frac{n}{N}$,

and
$$ln\frac{p_0}{p}=\frac{n}{N} \quad \text{or} \quad \frac{p_0-p}{p_0}=\frac{n}{N},$$

where $\frac{n}{N}$ is the ratio of the number of molecules of dissolved substance to the number of molecules of solvent This is the form in which Raoult empirically established the law of vapour pressure lowering in dilute solutions

Elevation of boiling point or depression of freezing point now becomes

$$\Delta\theta=\frac{\pi\theta}{1000\rho l}=\frac{cR\theta^2}{1000\rho l}$$

where l is either the latent heat (per gram) of vaporisation, or of fusion of the solvent

An important quantity, practically, is Raoult's 'Molecular Elevation of Boiling Point,' or 'Molecular Lowering of Freezing Point' The same derivation applies to either, provided l is given the appropriate meaning We may therefore consider the 'Molecular Lowering of Freezing Point' only

This is defined as the depression of the freezing point which would be caused by one gram molecule of the solute dissolved in 100 grams of the solvent It is therefore the value of $\Delta\theta$ for this value of c

c, however, must be measured in gram molecules per litre We must, therefore, find to what one gram molecule in 100 grams corresponds when expressed in gram molecules per litre

1 gram molecule in 100 grams solvent$\equiv$10 gram molecules in 1000 grams of solvent

$\equiv 10\rho$ gram molecules in 1000 c cs of solvent, where ρ=density of solvent

Thus, c, in the above formula, must be 10ρ, $\Delta\theta$ will then be K, the 'molecular lowering'

$$K=\frac{10\rho R\theta^2}{1000\rho l}=\frac{R\theta^2}{100l}=\frac{02\theta^2}{l},$$

since R=2 calories (measured in the same units as l).

MORE CONCENTRATED SOLUTIONS

In concentrated solutions the osmotic pressure is found to be greater than that calculated from van't Hoff's law Since the vapour pressure lowering, the elevation of boiling point and the depression of freezing point are all directly proportional to the osmotic pressure, these will, in the case of more concentrated solutions, all be greater than the values calculated from the equations just established for dilute solutions According to the van't Hoff relation $\pi = cR\theta$, the osmotic pressure is directly proportional to the concentration Hence, for dilute solutions the depression of freezing point is proportional to concentration, but for more concentrated solutions doubling the concentration produces more than double the freezing point depression

Many equations have been suggested for the representation of the osmotic pressure of solutions which are not dilute In every instance, and despite occasional claims to the contrary, they depend upon the introduction of additional constants which have to be evaluated from the experimental data themselves In those depending upon hydration theories, for example, the degree of hydration has to be fixed *ad hoc*

The best of the one constant equations is that of Sackur,

$$\pi(V-b)=R\theta,$$

where b is an arbitrarily chosen constant The value of π found from this could be substituted in all the equations we have so far derived, which would then be applicable to much more concentrated solutions.

OSMOTIC PRESSURE AND GAS PRESSURE

It may be shown that if a certain condition is fulfilled, then the equality of osmotic pressure and gas pressure is a thermodynamic necessity. But the condition in question is already rather a specialised one, itself implying some sort of analogy between the behaviour of the solute and the behaviour of a gas It is that the solute behaves in accordance with Henry's law This law states that the concentration of a volatile solute in the solution bears a constant ratio to its concentration in the gas phase over the solution. For the purposes of the argument, all solutes, even those commonly regarded as completely non-volatile, have to be supposed to exist in small concentration in the gas phase as well as in solution If the concentration in this gas phase is directly proportional to that in solution, then the osmotic pressure exerted by the solute in solution must be equal to that which it would exert if present as a gas occupying the same volume

The proof depends upon a reversible isothermal cycle We previously had occasion to derive a relation between the osmotic pressure of the *solute* and the vapour pressure of the *solvent* Now we have to find a relation between the osmotic pressure and the vapour pressure both of the solute The procedure must therefore be modified By comparing carefully the following cycle with that used in finding the lowering of vapour pressure some insight may be gained into the method of devising cycles for particular purposes

We think of the solvent as non-volatile, or separated from the vapour region by a membrane permeable only to the vapour of the solute There is also a semi-permeable membrane which lets through liquid solvent but not solute.

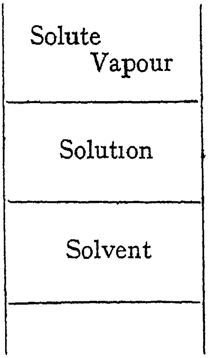

FIG 8

The osmotic pressure of the solute in solution is π

The pressure of the solute in the vapour phase is p_0

The following cycle is carried out

(1) A volume V of solvent, which would have contained a gram molecule of solute, is separated osmotically from the solution The work done on the system is πV π does not alter during this operation because simultaneously a gram molecule of solute is allowed to vaporise from the solution under the pressure p_0 Let this occupy the volume v_0 The system does work $p_0 v_0$ p_0 remains constant, since the osmotic

separation of solvent and the vaporisation of solute are carefully balanced so that the concentration of the remaining solution is left unchanged

The total work done by the system is thus $p_0v_0-\pi V$ in this stage

(ii) The solute vapour is expanded from v_0 to an indefinitely large volume v_∞ The system thereby does work

$$R\theta\, ln\frac{v_\infty}{v_0}$$

(iii) It can now be placed in contact with the pure solvent separated in (i), and reversibly compressed into it The work done on the system is

$$\int_0^{v_\infty} pdv$$

We require to know the value of p at any stage It is not given by $pv=R\theta$, since some of the original gram molecule has actually gone into the liquid This is where Henry's law comes in

If the volume V of liquid contained 1 gram molecule of solute, the pressure in the gas phase would be p_0 When the pressure is p, it means that the amount in solution is $\frac{p}{p_0}$ of a gram molecule. Thus, the amount still undissolved is $\left(1-\frac{p}{p_0}\right)$ gram molecules

Since $\quad pv=nR\theta$ for n gram molecules,

therefore $\quad pv=\left(1-\frac{p}{p_0}\right)R\theta$; whence $p=\frac{p_0R\theta}{(R\theta+p_0v)}$.

Therefore
$$\int_0^{v_\infty} pdv=p_0R\theta\int_0^{v_\infty}\frac{dv}{R\theta+p_0v},$$
$$=\frac{p_0R\theta}{p_0}ln\frac{(R\theta+p_0v_\infty)}{R\theta},$$
$$=R\theta\, ln\left(1+\frac{p_0}{R\theta}v_\infty\right).$$
$$=R\theta\, ln\left(1+\frac{v_\infty}{v_0}\right).$$

since
$$\frac{p_0}{R\theta}=\frac{1}{v_0}$$

We now have the *status quo*

The work done by the system in stages (ii) and (iii) is

$$R\theta\, ln\frac{v_\infty}{v} - R\theta\, ln\left(1+\frac{v_\infty}{v_0}\right),$$

or

$$-R\theta\, ln\frac{1+\frac{v_\infty}{v_0}}{\frac{v_\infty}{v_0}} = -R\theta\, ln\left(\frac{v_0}{v_\infty}+1\right),$$

$$= -R\theta\left(\frac{v_0}{v_\infty} - \frac{1}{2}\left(\frac{v_0}{v_\infty}\right)^2 \cdots\right),$$

$$=0$$

Since $\frac{v_0}{v_\infty}$ may be made as small as we please

Thus the net work done in the cycle is $p_0v_0 - \pi V$

This must by the second law of thermodynamics be zero

Therefore $p_0v_0 = \pi V$ This is the desired result

It is to be noted that Henry's law had to be introduced in stage (iii) If another law had been used the work terms in (ii) and (iii) would not have cancelled

THE NATURE OF OSMOTIC PRESSURE

In a strictly formal treatment of thermodynamics the discussion of this problem would be out of place But since it is desirable to keep the molecular basis of the thermodynamical laws as clear as possible, and since the osmotic pressure is the simplest measure of the diffusion tendency to which thermodynamical reasoning can be applied, it will be worth while to discuss briefly the molecular side of the subject It is also interesting to compare the rigidly thermodynamical method with the method of more direct attack Any deductions which may be made from the second law of thermodynamics about a particular phenomenon must depend only on the general molecular kinetic character of the phenomenon in question, and not on its specific nature It is obvious therefore that thermodynamics cannot provide a complete solution in general, it is indeed remarkable that detailed properties are so closely defined as they frequently are by the general principles

With regard to osmotic pressure, we have seen that the laws of thermodynamics yield the following information

(1) If the heat of further dilution of the solution by solvent is negligibly small, the osmotic pressure is directly proportional to the absolute temperature

(2) If the concentration of the solute in solution may be regarded as directly proportional to its concentration in the vapour over the solution (Henry's law), then the osmotic pressure is equal to the gas pressure, and given by the equation $\pi V = R\theta$

(3) When the solution is not too concentrated the relative lowering of vapour pressure, elevation of boiling point, and depression of freezing point of the solvent are directly proportional to the osmotic pressure of the dissolved substance

These results are of course independent of the specific mechanism of osmotic pressure

It must also be remembered that we started by assuming the existence of osmotic pressure as an experimental fact We could have started by taking the lowering of vapour pressure as the experimental fact, and inferred from this that work must be done in separating solvent from solution by a semi-permeable membrane, thus discovering the existence of an osmotic pressure But one or other had to be assumed first We will now consider the kinetic theory both of osmotic pressure and of vapour pressure lowering, we will take vapour pressure lowering first.

Consider unit area of the surface of separation of liquid solvent and vapour During each second a certain fraction of all the molecules in the surface of the liquid acquire by collisions a sufficiently large outwardly directed velocity to escape from the liquid into the vapour space in spite of the attractive forces holding them in the liquid During each second a number of molecules from the vapour space impinge upon the surface of separation, and of these a certain fraction condense Since, moreover, the number of impacts of molecules from the vapour on the surface of the liquid is proportional to their concentration in the vapour phase, we have

Number of molecules evaporating $= k_1 \times$ number of molecules of solvent present in unit area of the surface

$$= k_1 N$$

Number of molecules condensing $= k_2 \times$ concentration of molecules in vapour space

k_1 is smaller the smaller the fraction of the total number which evaporate per second, it is therefore smaller the greater the attractive forces which retain the molecules

For equilibrium at constant temperature the rate of evaporation must be equal to the rate of condensation

Therefore,

$$k_1 \times N = k_2 \times \text{concentration in vapour space} = k_3 \times \text{pressure of vapour,}$$

$$= k_3 p_0$$

Thus at equilibrium $k_1 N = k_3 p_0$, or $p_0 = \frac{k_1 N}{k_3}$

Since N is constant at constant temperature, the vapour pressure p_0 is constant

Now consider unit area of the surface of separation of solution and vapour Since we are dealing with the partial pressure of the solvent vapour we may simplify matters by regarding the solute as non-volatile The vapour pressure of the solvent is now no longer given by

$$p_0 = \frac{k_1 N}{k_3} \text{ but by } p = \frac{k_1' N'}{k_3'},$$

each one of the quantities being modified by the presence of the solute in a way which must be determined

N' will in general be less than N since a certain proportion of the molecules in the surface of separation are solute molecules which either do not evaporate, or if they do evaporate contribute nothing to the partial pressure of the solvent vapour This tends to reduce p as compared with p_0 In the case of a solution, k_1' is dependent on two factors, one referring to molecules of the solvent which are out of the range of the attractive forces of the solute molecules, and one referring to those which are within that range In the case of a dilute solution the first factor will predominate tending to keep k_1' the same as k_1, but whether those molecules within range of the attractive forces of the solute molecules evaporate more frequently or less frequently depends upon whether the attractive force between a solute and a solvent molecule is smaller or greater than that between two solvent molecules There are many independent reasons for believing it to be greater Thus the net result will be a value of k_1' which is slightly less than k_1 This again operates in the direction of a lowered vapour pressure k_3' will be rather greater than k_3, since the number of impacts of vapour molecules on the surface of separation is unchanged while the proportion leading to condensation is probably slightly greater owing to the superior attraction of solute molecules for solvent molecules This also leads to a lower value of p It is possible that N' might be greater than N if a very large contraction in volume accompanied solution, so that the volume occupied by the solution was actually less than that occupied by the solvent This, however, could only come about as a result of very large attractive forces between solvent and solute The diminution in k_1' would in this case be so great as completely to outweigh any increase in N'

It will be seen that even this incomplete and qualitative discussion has involved us in assumptions about the nature of solutions which did not enter into the thermodynamic calculations But we are going rather beyond the scope of the original inquiry which was not to ascertain the fact of vapour pressure lowering, but merely the relation between an assumed lowering and an inferred osmotic pressure, or an assumed osmotic pressure and an inferred lowering of vapour pressure

Given, however, the circumstances which we have postulated to explain the lowering of vapour pressure we can explain kinetically the existence of osmotic pressure also. For consider unit area of a semi-permeable membrane, with solvent on one side and solution on the other The mechanism of the membrane does not matter, it is not probable that all semi-permeable membranes work in the same way We may, however, for the sake of a concrete example, suppose its action to be due to selective solubility It dissolves solvent but not solute *Mutatis mutandis*, the following argument would apply to any other kind of semi-permeable membrane Equilibrium is established when the number of solvent molecules entering the membrane from the solvent side is equal to the number leaving the membrane on that side, and when also the number entering the membrane on the solution side is equal to the number leaving it on that same side The molecules of solvent which dissolve in the membrane are those which impinge upon it possessing sufficient energy to overcome the forces holding them in the liquid This number is smaller on the solution side of the membrane for precisely those reasons which cause the lowering of vapour pressure, namely because the number present per unit area is less, owing to the presence of the solute, and because some are held back more firmly owing to the superior attractive force between solute and solvent However the relative weight of these two factors may vary, it will vary in the same way in the case of vaporisation as in the case of entrance into the semi-permeable membrane If a larger number of solvent molecules enter the membrane from the solvent side than from the solution side there will not be equilibrium, solvent will stream through the membrane into the solution The pressure which must be applied to prevent its entry is the osmotic pressure

Lowering of freezing point will be illustrated kinetically when we come to consider the phase rule

In the present state of knowledge regarding the forces between molecules in solutions it has not been found possible to calculate the actual magnitude of the osmotic pressure on the basis of the theory just outlined Van't Hoff attacked the problem in a way which although not free from objection is not at variance with the foregoing He attributed the osmotic pressure to the bombardment of the membrane by the solute He assumed that the kinetic energy of the solute molecules is on the average that which they would possess in the gaseous state at the same temperature This is confirmed by the experiments of Perrin, who, by extending the thesis even to colloidal particles, has justified the assumption by making with its aid fairly accurate determinations of the number of molecules in a gram molecule When the solution is sufficiently dilute for solute molecules to be without influence on one another this leads to the result that the solute should obey the gas laws The application of this law of van't Hoff we have already seen

It is easily seen that the bombardment pressure of the solute is identical with the osmotic pressure, defined as the pressure which must be applied to the solution to prevent inflow of solvent through the semi-permeable membrane. Imagine solvent and solution to be separated by a membrane which is not permeable to either No resultant pressure is exerted upon it which would urge it to move through the liquid in any direction The pressures on each side are equal. Pressure cannot be exerted by a liquid by any means other than molecular bombardment Thus the total bombardment pressure on solvent side = total bombardment pressure on solution side = bombardment pressure due to solvent molecules + bombardment pressure due to solute molecules

Therefore,

Pressure due to solvent molecules on solvent side of membrane — Pressure due to solvent molecules on solution side of membrane
=bombardment pressure due to solute molecules

The left hand side of this equation is the pressure which would urge the solvent through the membrane if the latter were semi-permeable, and is therefore the pressure which must be applied to the solution to stop the solvent from entering, that is the osmotic pressure Thus osmotic pressure =bombardment pressure of solute

The following difficulty is sometimes felt, and is only mentioned here because remarkably enough it is not confined to elementary students If an applied hydrostatic pressure can prevent the entry of solvent why cannot the bombardment pressure of the solute ? Why in fact is the osmotic pressure not exerted the other way round ? This difficulty depends of course upon a complete misunderstanding of the kinetic nature of pressure, and the explanation is simple The difference between the bombardment pressures of the solvent on the two sides of the membrane measures its tendency to flow through, because the bombardment pressure on a given side of the membrane is proportional to the number of molecules which strike it, and therefore in turn to the number which pass through If there is any difference on the two sides it means actually that more molecules of solvent are streaming one way than the other way This, of course, cannot be balanced by independent collisions of a foreign substance, the solute, on the membrane On the other hand a hydrostatic pressure, whether exerted by a piston or by gravity, is transmitted by collisions through the solvent itself, and thus increases the actual solvent bombardment on the membrane until it is equal to the bombardment on the pure solvent side (Incidentally the solute bombardment is also increased , by entering into refinements in the thermodynamics of osmotic pressure it may indeed be shown that the osmotic pressure is in fact slightly influenced by the total hydrostatic pressure) There is now osmotic equilibrium , but the membrane is now no longer in hydrostatic equilibrium, and unless rigidly supported would move through the liquid The whole matter becomes clear when it is once realised that osmotic equilibrium and hydrostatic equilibrium are not consistent with one another

THERMODYNAMIC RELATIONS CONNECTED WITH SOLUBILITY. (*a*) THE PARTITION LAW

The free energy principle may be applied to derive the well-known Partition law of Nernst, according to which a dissolved substance distributes itself between two immiscible solvents in a constant concentration ratio, provided that its molecular condition is the same in both solvents, and that the concentrations are sufficiently low for van't Hoff's osmotic law to hold

If the gram molecular concentrations of the solute in the two solvents are C_1 and C_2 in one case, and C_1' and C_2' in a second case, then $\frac{C_1}{C_2}=\frac{C_1'}{C_2'}$.

Suppose the substance in the first solvent be diluted osmotically and reversibly from concentration C_1 to concentration C_1' The decrease in free energy per gram molecule will be $\int_{V_1}^{V_1'}\pi dV$,

where π is the osmotic pressure and V_1' and V_1 are the volumes containing a gram molecule, i e the reciprocals of C_1' and C_1

Since $\pi V=R\theta$ the free energy change is

$$R\theta\int_{V_1}^{V_1'}\frac{dV}{V}=R\theta\, ln\frac{V_1'}{V_1},$$

$$=R\theta\, ln\frac{C_1}{C_1'}$$

If the substance in the second solvent be diluted in the same way from concentration C_2 to C_2', the free energy decrease is $R\theta\, ln\frac{C_2}{C_2'}$

When the concentrations in the first and second solvent are C_1 and C_2 respectively the two layers are in equilibrium When the concentrations are C_1' and C_2' they are still in equilibrium Hence the decrease in free energy accompanying the dilution of the solute in the first solvent from C_1 to C_1' must be equal to the decrease in free energy accompanying the dilution from C_2 to C_2' in the second solvent

Therefore

$$R\theta\ ln\frac{C_1}{C_1'}=R\theta\ ln\frac{C_2}{C_2'},$$

or

$$\frac{C_1}{C_1'}=\frac{C_2}{C_2'},\ \text{and}\ \frac{C_1}{C_2}=\frac{C_1'}{C_2'}$$

(*b*) SOLUBILITY OF STABLE AND UNSTABLE FORMS

When a substance exists in more than one modification the unstable form has the higher vapour pressure, and the decrease in free energy associated with the transition of a gram molecule of the unstable into the stable form is $R\theta\ ln\frac{p_1}{p_2}$

Solubility is in many ways analogous to vapour pressure The vapour pressure of a solid substance measures the concentration of that substance in the space over the solid when the number of molecules leaving the solid surface in unit time is equal to the number returning The solubility, in a similar way, is the concentration in a solution when the number of molecules leaving the solid surface is equal to the number returning Since the unstable form has the greater solubility its saturated solution is supersaturated with respect to the stable form, so that if stable and unstable are present together in contact with solution the unstable continuously goes into solution while the stable form grows at its expense In solution, of course, the substance exists in one form only

The free energy of transformation may be calculated as follows

Let the unstable form be in contact with its saturated solution, bounded by a semi-permeable membrane outside which is solvent We cause one gram molecule to dissolve by moving the semi-permeable membrane outward The work done is $\pi_1 V_1$, π_1 being the osmotic pressure of the saturated solution of the unstable form, and V_1 that volume (in litres) which contains one gram molecule

The solution of the one gram molecule is removed from contact with the solid, and diluted osmotically to volume V_2 which is the volume in litres occupied by a gram molecule of the stable form

The work performed is $R\theta\ ln\frac{V_2}{V_1}$ The osmotic pressure is now π_2

We now place this solution in contact with the stable form and cause a gram molecule to be precipitated by moving in the semi-permeable piston so that V_2 of solvent is removed Work $\pi_2 V_2$ is now performed on the system, which cancels the work $\pi_1 V_1$ performed by the system when the unstable form was caused to dissolve

The net work performed by the system in the whole process is $R\theta \; ln\frac{V_2}{V_1}$

Since V_2 and V_1 are the volumes in litres which contain a gram molecule of the substance when the solution is saturated with respect to stable and unstable forms respectively, they are the reciprocals of the gram molecular solubilities S_2 (stable) and S_1 (unstable)

Thus
$$A = R\theta \; ln\frac{S_1}{S_2}$$

Since we have used van't Hoff's law, this relation is only strictly true when both the solubilities are small, so that the saturated solutions are not very concentrated

CONCENTRATION CELLS

It should be obvious how by an exactly similar method the electromotive force of a concentration cell, where both solutions are dilute enough to be completely ionised, is found to be given by the equation

$$nEF = R\theta \; ln\frac{C_1}{C_2}$$

When the two solutions are not completely ionised the derivation of a formula is rather complicated The equation

$$nEF = R\theta \; ln\,\frac{\alpha_1 C_1}{\alpha_2 C_2},$$

α_1 and α_2 being the respective 'degrees of ionisation' in the two solutions, is only approximately correct—quite apart even from the complications resulting from the 'anomaly of strong electrolytes'

THE LAW OF MASS ACTION

The fundamental form of the law of mass action which relates the velocity of a chemical change to the concentration of the reacting substances is not deducible from the laws of thermodynamics The derived form which gives the equilibrium constant as a function of the several concentrations may be derived at once by an application of the free energy principle

In Chapter IV we considered the device of the equilibrium box, and found that the work performed at temperature θ when a gram molecule each of carbon monoxide and water at the concentrations respectively C_1 and C_2 gram molecules per litre are converted reversibly into carbon dioxide and hydrogen at concentrations C_3 and C_4 respectively is given by

$$A=R\theta\left\{ln\frac{C_1C_2}{C_3C_4}-ln\frac{c_1c_2}{c_3c_4}\right\},$$

where c_1, c_2, c_3 and c_4 are the concentrations respectively of the different gases in equilibrium in the equilibrium box at the temperature θ

c_1, c_2, c_3, c_4 are not unique values for the concentrations They were selected from an indefinite number of possible equilibrium values

Let us now alter the concentrations in the equilibrium box itself by adding more of one or other of the gases The equilibrium will be disturbed and a new one established where the concentrations are c_1', c_2', c_3' and c_4'

The equilibrium box is still just as effective as a means of converting the gram molecules of CO and H_2O reversibly into CO_2 and H_2 Let exactly the same process as before be carried out with the new box, namely the conversion of a gram molecule of carbon monoxide and of water vapour at concentrations C_1 and C_2 into carbon dioxide and hydrogen at concentrations C_3 and C_4 The free energy change is now

$$A=R\theta\left[ln\frac{C_1C_2}{C_3C_4}-ln\frac{c_1'c_2'}{c_3'c_4'}\right]$$

But it has been established that the free energy change accompanying the passage of a system from one state to another is independent of the particular reversible path for which it is calculated Therefore,

$$R\theta\left[ln\frac{C_1C_2}{C_3C_4}-ln\frac{c_1c_2}{c_3c_4}\right]=R\theta\left[ln\frac{C_1C_2}{C_3C_4}-ln\frac{c_1'c_2'}{c_3'c_4'}\right],$$

whence
$$\frac{c_1c_2}{c_3c_4}=\frac{c_1'c_2'}{c_3'c_4'},$$

Similarly
$$\frac{c_1c_2}{c_3c_4}=\frac{c_1''c_2''}{c_3''c_4''}$$

In other words,

$$\frac{\text{concentration of } CO \times \text{concentration of } H_2O}{\text{concentration of } CO_2 \times \text{concentration of } H_2} = \text{constant}$$

The result is easily generalised

If the reaction is of the general form

$$n_1A_1+n_2A_2+ \qquad =n_1'B_1+n_2'B_2$$

which means that n_1 molecules of a substance A_1+n_2 of A_2, etc , react to give n_1' of B_1, etc , then we proceed as follows

We imagine an equilibrium box containing the substance A_1, A_2 and B_1, B_2 in equilibrium proportions—an indefinite number of such systems in equilibrium exist We proceed to take n_1 molecules of A_1 at concentration C_1, n_2 of A_2 at C_2, and so on, and calculate the free energy change when they are transformed into n_1' molecules of B_1 at concentrations C_1' and so on C_1, C_2 , C_1', etc , are quite arbitrarily chosen

The method is precisely the same as that used for the water gas reaction We take the appropriate number of molecules of each substance of the left hand side of the equation, and alter their several concentrations until they become respectively the same as those in the equilibrium box At these equilibrium concentrations the substances on the left of the equation are introduced through the appropriate windows into the box, the substances on the right of the equation being simultaneously removed in stoicheiometrically equivalent amounts at the respective equilibrium concentrations Their concentrations are now altered until they attain the desired arbitrary values C_1', etc

To calculate the work performed by the system in this process let us take a typical substance from the left hand side of the equation; initial concentration C, concentration in equilibrium box c Number of molecules appearing in the equation n The work performed by the system when n molecules are brought from concentration C to concentration c is $nR\theta \, ln\frac{C}{c}$ C is placed in the numerator since if $C>c$ the fraction $\frac{C}{c}>1$, the logarithm is then positive as it should be since positive work is performed by the system when it passes from a higher to a lower concentration Each substance contributes a similar term

For the whole of the left hand side of the chemical equation we may thus write

$$\text{Work performed} = \Sigma nR\theta \, ln\frac{C}{c}$$

In a similar way the work done by the system during the alteration of the typical substance on the right of the equation from the equilibrium concentration c' to the arbitrary final concentration C' is $n'R\theta \, ln \frac{c'}{C'}$, c' now being in the numerator since the work performed is positive when $c' > C'$. For all the substances the work sums up to

$$\Sigma n'R\theta \, ln\frac{c'}{C'}$$

Thus $$A = \Sigma nR\theta \, ln\frac{C}{c} + \Sigma n'R\theta \, ln\frac{c'}{C'}$$

In addition to this an amount of work $(n'-n)R\theta$ is performed by the system, since n' gram molecules have to leave the equilibrium box for n that enter This, being simply due to the total volume change accompanying the reaction, is not included in A for the present purpose

The above value of A may be written

$$A = \Sigma nR\theta \, ln\frac{C}{c} - \Sigma n'R\theta \, ln\frac{C'}{c'}$$

If we agree automatically to count the values of n' for substances on the right of the chemical equation as negative this may be simply written,

$$A = R\theta \Sigma n \, ln\frac{C}{c},$$

$$= R\theta \{\Sigma n \, ln \, C - \Sigma n \, ln \, c\}$$

We may proceed from our arbitrary initial state to an arbitrary final state *viâ* an equilibrium box in which any of the indefinite number of sets of equilibrium concentrations prevail In each case A will have the same value.

Thus $$\Sigma n \, ln \, c = \text{constant} = ln \, K,$$

and $$A = R\theta \{\Sigma n \, ln \, C - ln \, K\}$$

Since $$ln \, K = \Sigma n \, ln \, c$$

$$K = \frac{c_1^{n_1} c_2^{n_2} c_3^{n_3}}{c'^{\,n_1'}_1 \, c'^{\,n_2'}_2 \, c'^{\,n_3'}_3}$$

the general form of the equilibrium constant

APPLICATION OF THE GIBBS-HELMHOLTZ EQUATION

An important relation is found by substituting the value of A just obtained in the general equation $A-U=\theta\frac{dA}{d\theta}$

$$A=R\theta\{\Sigma n\ ln\ C-ln\ K\}$$

Therefore

$$R\theta\{\Sigma n\ ln\ C-ln\ K\}-U=\theta\frac{d}{d\theta}\{R\theta(\Sigma n\ ln\ C-ln\ K)\},$$

where U=heat of reaction at constant volume

$$R\theta\Sigma n\ ln\ C-R\theta\ ln\ K-U=\theta\left\{R\Sigma n\ ln\ C-R\theta\frac{d\ ln\ K}{d\theta}-R\ ln\ K\right\}$$

Since the terms constituting $\Sigma\nu\ ln C$ are arbitrarily chosen they can be treated as constant during the differentiation with respect to θ

Therefore $$-U=-R\theta^2\frac{d\ ln\ K}{d\theta},$$

$$\frac{d\ ln\ K}{d\theta}=\frac{U}{R\theta^2}$$

This equation connects the variation of the equilibrium constant with the temperature and the heat of reaction It will be discussed at length later on , it need only be pointed out here that U, being the decrease in total internal energy, is the heat *given out* when the reaction proceeds from left to right, and that K is constituted with the concentration terms referring to substances on the left of the chemical equation in the *numerator*, i e counted as *positive* in $\Sigma n ln c$

APPLICABILITY OF THE LAW OF MASS ACTION

In the foregoing derivation of the law of mass action for gaseous systems all the work terms were calculated on the assumption that the gases behaved in accordance with Boyle's Law The results therefore are only strictly valid for systems composed of such gases The equilibrium box device can be applied to dilute solutions, all concentration alterations being effected osmotically When van't Hoff's law applies to the solutions the law of mass action will therefore apply also

CHAPTER VI

ENTROPY AND THERMODYNAMIC FUNCTIONS CONDITIONS OF EQUILIBRIUM

WE have seen that when a system passes from one state to another at constant temperature a quantity, the maximum work has a quite definite value, whatever be the actual path by which the system proceeds from its initial to its final condition This result was arrived at by showing that unless the maximum work were the same for all isothermal reversible paths a cycle could be devised exempt from the consequences of the second law of thermodynamics The significance of the free energy has been illustrated We have now to consider another function, the entropy of a system It involves a more abstract idea than maximum work or free energy, at least in the form in which it is derived from the second law of thermodynamics, but it leads to the expression of the second law in a form which will subsequently be seen to represent very clearly the molecular meaning of the law.

We begin by returning once more to the Carnot cycle The four stages in this cycle are (1) an isothermal change involving the absorption of a quantity of heat Q_1 from a source of heat at the temperature θ_1, (2) an adiabatic change, (3) an isothermal change similar to (1), but in the opposite sense attended by the rejection of a quantity of heat Q_2 to a thermostat at the temperature θ_2, (4) an adiabatic change bringing the system back to its initial state For a perfect gas it is found that

$$\frac{Q_1-Q_2}{Q_1}=\frac{\theta_1-\theta_2}{\theta_1}$$

Carnot's theorem, depending upon the second law, then shows that for any analogous system this result is true

Since $$\frac{Q_1-Q_2}{Q_1}=\frac{\theta_1-\theta_2}{\theta_1}, \quad \frac{Q_1}{\theta_1}-\frac{Q_2}{\theta_2}=0$$

Q_1 is the heat absorbed by the system at θ_1, while Q_2 is that rejected at θ_2, or otherwise $-Q_2$ is that absorbed at θ_2 This relation may therefore be written

$$\frac{\text{heat absorbed at }\theta_1}{\theta_1}+\frac{\text{heat absorbed at }\theta_2}{\theta_2}=0,$$

for the cycle This applies generally to any cycle which is split up into isothermal and adiabatic parts It is desirable, however, to find a more general result, which will apply to all reversible cycles whether the isothermal and adiabatic stages are sharply separated or not In the most general case the heat which is absorbed is not exclusively employed in the performance of external work, as in the case of the isothermal expansion of a perfect gas, or in the increase of molecular potential energy, as in fusion or vaporisation, but some appears as increased molecular kinetic energy Heat is absorbed and the temperature of the system rises.

During the course of a cycle other than the simple Carnot cycle, a net amount of heat will have been absorbed, but at a continuously varying temperature, and a net amount of heat will have been rejected also at a continuously varying temperature In this case we cannot write simply

$$\frac{\text{heat absorbed at }\theta_1}{\theta_1}+\frac{\text{heat absorbed }\theta_2}{\theta_2}=0$$

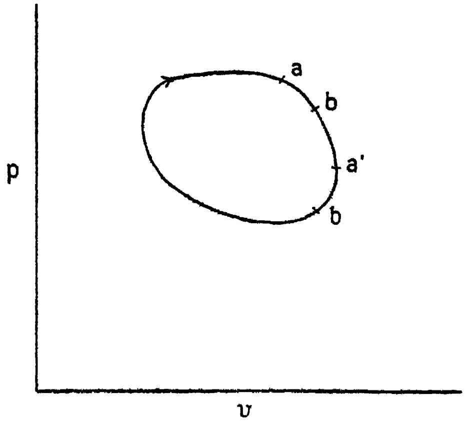

FIG 9

Consider the closed cycle shown in the figure Let *ab* be an element of path in which the volume increases, the pressure falls, the internal energy of the substances changes, and the temperature changes from θ to $\theta+d\theta$, the heat absorbed is dQ $d\theta$ and dQ may be positive or negative The element of path ab may be resolved into an isothermal and an adiabatic component The isothermal component involving the absorption of dQ at θ

The whole cycle may be split up into elements such as ab and $a'b'$ Let the lengths of the elements be chosen so that as many have a positive dQ as a negative dQ Then the second law of thermodynamics which led in the simple Carnot type of cycle to the form of relation,

$$\frac{\text{heat absorbed at }\theta_1}{\theta_1}+\frac{\text{heat absorbed at }\theta_2}{\theta_2}=0,$$

now takes the form

$$\Sigma\frac{\text{heat absorbed at }\theta}{\theta}(+ve)+\Sigma\frac{\text{heat absorbed at }\theta}{\theta}(-ve)=0,$$

or $$\int\frac{dQ}{\theta}=0,\text{ for the closed cycle}$$

A more rigid method of arriving at this generalisation is as follows

Let a cycle involve the absorption of q_1 at θ_1, q_2 at θ_2, q_3 at θ_3, q_4 at θ_4 from sources at the corresponding temperatures, and the rejection of q_1' at θ_1', q_2' at θ_2', etc, to reservoirs at these temperatures

Now let us have two auxiliary reservoirs, one at a temperature T, higher than any of the values θ_1, θ_2 , and the other at a temperature T', lower than any of the values θ_1', θ_2', etc

The carrying out of the cycle has left changes in all the reservoirs, which we can counteract by employing the auxiliary reservoirs Thus the source at θ_1 had lost q_1 We restore this by allowing a Carnot cycle to be carried out between the auxiliary source at T and the reservoir at θ_1 If the latter gains q_1 the former must lose an amount x_1 given by

$$\frac{x_1}{T}=\frac{q_1}{\theta_1},$$

whence $$x_1=\frac{q_1T}{\theta_1}$$

Similarly, to restore q_2, q_3, etc., to the various reservoirs the auxiliary one must lose

$$x_2 = \frac{q_2 T}{\theta_2}, \quad x_3 = \frac{q_3 T}{\theta_3}, \text{ etc.}$$

It loses altogether

$$Q = x_1 + x_2 + x_3 \qquad = T\left[\frac{q_1}{\theta_1} + \frac{q_2}{\theta_2} + \frac{q_3}{\theta_3} + \qquad\right]$$

In an analogous manner the gains q_1', q_2' , etc., can be neutralised by the aid of the auxiliary reservoir at T', which will in the process gain an amount of heat Q', given by

$$Q' = x_1' + x_2' + x_3' \qquad = T'\left[\frac{q_1'}{\theta_1'} + \frac{q_2'}{\theta_2'} + \qquad\right]$$

Thus the original cycle with its many stages is equivalent to a Carnot cycle in which Q is lost by a reservoir at T and Q' gained by a reservoir at T'.

Since $$\frac{Q}{T} - \frac{Q'}{T'} = 0,$$

we have also that

$$\left[\frac{q_1}{\theta_1} + \frac{q_2}{\theta_2} \qquad\right] - \left[\frac{q_1'}{\theta_1'} + \frac{q_2'}{\theta_2'} \qquad\right] = 0$$

from the values of Q and Q'.

If we agree that heat rejected shall be regarded as a negative contribution to the heat absorbed, we may write this last equation as $$\Sigma \frac{q}{\theta} = 0,$$

and when the magnitude of the values q_1, q_2, etc., is diminished indefinitely and their number multiplied indefinitely, this becomes $$\int \frac{dQ}{\theta} = 0$$

This is a most important relation. It is directly derived from the second law of thermodynamics simply by generalising the efficiency theorem. It will be instructive, however, to see, qualitatively at least, how it embodies the fundamental idea of the second law. This may best be done by seeing how the integral $\int \frac{dQ}{\theta}$ compares with $\int dQ$. When the cycle is traversed in the direction of the arrow the system performs work equal to the area of the cycle. Since, moreover, the cycle is a closed one, the substance returning in every respect to its initial state with its internal energy unchanged, this work which is performed must be equal to the net amount of heat absorbed $=\int dQ$.

$\int dQ$ is therefore a positive quantity. An integral is the sum of a number of infinitesimal terms. Of the terms constituting $\int dQ$ the positive ones must therefore sum up to a greater value than the negative ones. This is simply the first law. The second law tells us, however, that the performance of work at the expense of heat must be compensated in a case like this by the simultaneous passage of some heat from a reservoir at a higher to one at a lower temperature. This means that all the positive elements in $\int dQ$ are associated with higher values of θ than the negative elements. Thus, we have $\int$positive dQ elements $>\int$negative dQ elements or $\int dQ$ is positive, but in the $\int\frac{dQ}{\theta}$, the larger positive dQ elements are divided by larger values of θ than the smaller negative elements. Hence, while $\int dQ$ must be positive, $\int\frac{dQ}{\theta}$ need not be, and the detailed investigation given above shows that in fact the actual value is zero.

We must now pay attention to an important difference between the quantity $\int dQ$, and quantities such as $\int d\theta$ and $\int dv$. Pressure, volume, temperature, and total internal energy are all quantities which define the actual state of a system. There is, however, no quantity Q such that a given value of Q corresponds to a given state of the system. A gas under given conditions has perfectly definite p, v, θ, and U values, but no characteristic value of Q. If the system changes the new state is defined by new values of p, v, θ, and U, which do not depend at all upon the manner in which the change of state of the system has come about. On the other hand, during the change a quantity of heat Q may have been absorbed or rejected, the value of which depends not only upon the difference between the initial and final states, but upon the exact path traversed. p, v, θ, and U are characteristic of the momentary state of the system; Q depends on the nature of the process by which the passage between two states is effected. Now suppose the system to traverse a closed reversible cycle. The system returns to its original condition; pressure, volume, temperature, and internal energy all regain their initial values. For the closed cycle, therefore, $\int dp=p-p=0$; $\int dv=0$; $\int d\theta=0$; $\int dU=0$.

On the other hand, $\int dQ$=work done during cycle=area of cycle, and is not in general zero, but a positive quantity Moreover, since it must be equal to $\int p dv$, it can only be evaluated in terms of p and v by knowing the relation of p and v at every point, so that p may be expressed in terms of v and the integration performed The integral $\int dQ$ thus depends upon the equation connecting p and v, that is, upon the shape of the p, v curve or the exact nature of the cycle

Let us now express $\frac{dQ}{\theta}$ by the symbol dS

Then for a closed reversible cycle $\int dS = \int \frac{dQ}{\theta} = 0$

dS thus resembles dp, dv, $d\theta$, and dU, in that its integral round a closed cycle is zero, not dQ, of which the integral round a closed cycle depends upon the shape of the path

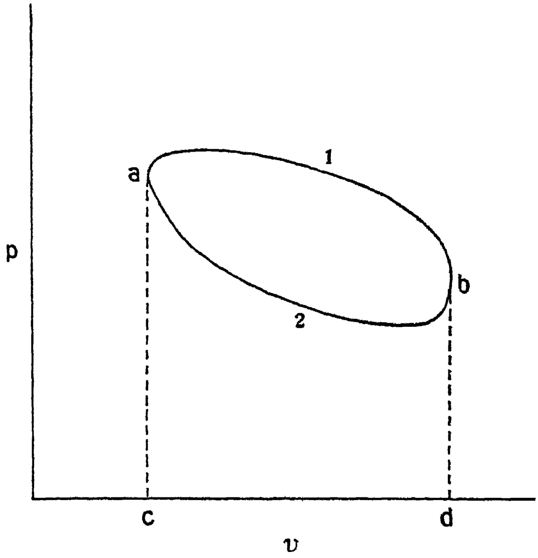

FIG 10

Therefore there must exist a quantity S characteristic of the momentary state of the system, just as p, v, θ, and U are characteristic of the state of the system S is not analogous to Q

which depends on the path by which the system changes and regains its initial state, but must regain its original value when the system returns to its original state Unlike Q, therefore, which is a function of the process of transfer, S is a characteristic *property* of the system This quantity S, whose existence has thus been inferred is called the *entropy* of the system

Let us now consider, not a complete cycle, but merely a reversible change from a state represented by the point a in the figure to one represented by b The external work performed is equal to the area $a1bcd$ if we proceed by the path $a1b$, and to the area $a2bcd$, if we proceed by the path $a2b$

By whichever path we proceed the change in pressure is p_b-p_a, the change in volume v_b-v_a, the change in temperature $\theta_b-\theta_a$, and the change in internal energy U_b-U_a

Thus $$\int_a^b dp=p_b-p_a, \text{ etc}$$

The $\int_a^b dQ$ cannot be written Q_b-Q_a, however, since it depends not only upon U_b and U_a, but also on the external work the amount of which clearly varies with the shape of the curve connecting a and b

With $\int_a^b \frac{dQ}{\theta}$, however, matters are different

Let $$\int_a^b \frac{dQ}{\theta} \text{ by path } 1=S_1,$$

and $$\int_a^b \frac{dQ}{\theta} \text{ by path } 2=S_2$$

Then, if the cycle $a1b2a$ be traversed, we have

$$\int\frac{dQ}{\theta}=0 \quad \text{and} \quad \int\frac{dQ}{\theta}=S_1-S_2$$

Thus $$S_1=S_2$$

By whatever path, therefore, we proceed the $\int\frac{dQ}{\theta}$ is the same, i e depends only on the position of b and a Thus once more we see that there is a function S characteristic of the state of the system at each point, and just as $\int_a^b dp=p_b-p_a$, so $\int_a^b dS=S_b-S_a$ S_b being the entropy of the system at b, and S_a being the entropy of the system at a

PROPERTIES OF THE ENTROPY FUNCTION

In a reversible adiabatic change the entropy of the system remains unaltered Since neither absorption nor rejection of heat takes place at any point dQ is zero over every element of path, hence $\int_a^b\frac{dQ}{\theta}=0$, therefore $S_b=S_a$ Thus every point on an adiabatic curve represents a state of equal entropy, just as every point on an isothermal curve represents a state of equal temperature

In an isothermal change θ is constant Thus

$$\int_a^b\frac{dQ}{\theta}=\frac{1}{\theta}\int_a^b dQ=\frac{\text{heat absorbed in change}}{\theta}.$$

For example, when one gram of liquid evaporates at the constant temperature θ, the heat absorbed is λ, the latent heat of vaporisation, and the change in entropy of the system is

$$\frac{\lambda}{\theta}$$

ENTROPY OF A PERFECT GAS

We begin with the equation describing the fate of an elementary quantity of heat dQ added to a perfect gas,

$$dQ=C_v d\theta+pdv$$

Then to find the change in entropy when the gas passes from state a to state b, we have

$$S_b - S_a = \int_a^b \frac{dQ}{\theta} = \int_a^b \frac{C_v d\theta}{\theta} + \int_a^b \frac{p dv}{\theta}$$

$$= \int_a^b \frac{C_v d\theta}{\theta} + \int_a^b \frac{R dv}{v},$$

$$= C_v \, ln \frac{\theta_b}{\theta_a} + R \, ln \frac{v_b}{v_a}$$

We note, incidentally, that if the gas has traversed a closed cycle so that $b=a$, then

$$S_b - S_a = \int \frac{dQ}{\theta} = C_v \, ln \, 1 + R \, ln \, 1 = 0$$

Instead of integrating between limits b and a to find the change in entropy, we may now integrate without limits to find the general value of the entropy

$$\int \frac{dQ}{\theta} = S = C_v \, ln \, \theta + R \, ln \, v + constant$$

The integration constant is not determinate

v is the volume in litres which is occupied by one gram molecule of the gas

$v = \frac{1}{C}$ where C is the concentration of the gas in gram molecules per litre

Thus $\quad S = C_v \, ln \, \theta - R \, ln \, C + \text{constant}$

ENTROPY OF A MIXTURE OF PERFECT GASES

If two gases intermingle at constant pressure the entropy increases, since each now occupies the whole volume, namely, the sum of the two original volumes Suppose we have n_1 gram molecules of gas 1 and n_2 gram molecules of gas 2 at the same pressure The original entropies are respectively

$$n_1 \, [C_{v_1} \, ln \, \theta + R \, ln \, v] \text{ and } n_2 \, [C_{v_2} \, ln \, \theta + R \, ln \, v],$$

v being the volume occupied by one gram molecule of a perfect gas at the given pressure

After mixing, the total volume is $n_1 v + n_2 v$, and the volume occupied by one gram molecule of 1 is now

$$\frac{n_1 v + n_2 v}{n_1} = v\left(\frac{n_1 + n_2}{n_1}\right),$$

and the volume occupied by one gram molecule of gas 2 is

$$v\left(\frac{n_1+n_2}{n_2}\right),$$

thus the total entropy is

$$n_1\left[C^{v}{}_{1}\,ln\,\theta+R\,ln\left(\frac{n_1+n_2}{n_1}\right)v\right]+n_2\left[C_{v_2}\,ln\,\theta+R\,ln\left(\frac{n_1+n_2}{n_2}\right)v\right].$$

Calling the fractions $\frac{n_1}{n_1+n_2}$ and $\frac{n_2}{n_1+n_2}$, x_1 and x_2 we have for the entropy,

$$n_1\left[C_{v_1}\,ln\,\theta+R\,ln\,v-R\,ln\,x_1\right]+n_2\left[C_{v_2}\,ln\,\theta+R\,ln\,v-R\,ln\,x_2\right],$$

or generally $\quad \Sigma n[C_v\,ln\,\theta+R\,ln\,v-R\,ln\,x]$

CHANGE IN ENTROPY ASSOCIATED WITH REVERSIBLE AND IRREVERSIBLE PROCESSES

We have seen that for a closed reversible cycle $\int\frac{dQ}{\theta}=0$, and from this result have inferred the existence of a characteristic function the entropy such that for all reversible changes

$$\int_a^b\frac{dQ}{\theta}=S_b-S_a.$$

We have now to consider a point which requires a little care, and about which confusion sometimes exists S_b refers definitely to the state b of the substance, S_a to the state a S_b-S_a is therefore characteristic of the difference between the two states and no longer has any relation to the process by which transformation from one to the other takes place $\int\frac{dQ}{\theta}$, however, can never lose this relation in quite the same way, because the condition always remains that the change must be a *reversible* one in order that $\int\frac{dQ}{\theta}$ may be independent of the path We define S_b-S_a as the value of $\int\frac{dQ}{\theta}$ for a reversible path, knowing that for all reversible paths it has the same value When we pass from a to b by an irreversible path $\int_a^b\frac{dQ}{\theta}$ for the irreversible path has no longer the same constant value It no longer defines S_b-S_a, which remains as before, equal to the value which the integral *would have* for a reversible path Thus, for an irreversible process

$$\int_a^b \frac{dQ}{\theta}\text{ irrev} \neq S_b-S_a$$

The modification introduced into the relation by irreversibility is easily found The general equation for a complete reversible cycle, $\int \frac{dQ}{\theta}=0$, was found by extending the result found for a Carnot cycle

If an element of irreversibility is introduced at any stage of the Carnot cycle the efficiency will be lowered We shall no longer have $\frac{Q_1-Q_2}{Q_1}=\frac{\theta_1-\theta_2}{\theta_1}$, but $\frac{Q_1-Q_2}{Q_1}<\frac{\theta_1-\theta_2}{\theta_1}$, and when this is transformed as before we find the general relation to be $\int \frac{dQ}{\theta}<0$.

Since it is not always convenient to deal with complete cyclic processes, we need to know what modification to make in the differential relation $\frac{dQ}{\theta}=dS$ when the small element of path to which it refers represents an irreversible transformation This is most easily seen by considering the cycle $ABCD$ in which ABC represents an irreversible transformation

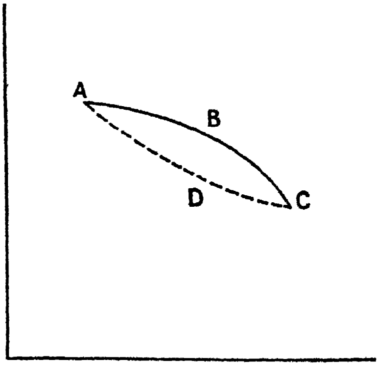

FIG 11

from A to C, while CDA represents a reversible path For the whole cycle $\int \frac{dQ}{\theta} < 0$, since as a whole it is irreversible But for the reversible path CDA, we have

$$\int_C^A \frac{dQ}{\theta} = S_A - S_C$$

Therefore, for the irreversible path ABC

$$\int_A^C \frac{dQ}{\theta} = \int^{\text{cycle}} \frac{dQ}{\theta} - (S_A - S_C)$$

Hence irr $\int_A^C \frac{dQ}{\theta} + (S_A - S_C) < 0.$

$$\int_A^C \frac{dQ}{\theta} < S_C - S_A.$$

Hence $\frac{dQ}{\theta} < dS,$

or $\theta dS > dQ,$

$\theta dS = dQ + \Delta$, where Δ is a positive quantity

This relation, as will be seen presently, is of great importance in determining the conditions of equilibrium of a system

If we have a system to which heat is not added and from which heat is not allowed to escape, then $dQ = 0$, then $\theta dS > 0$ for an irreversible change , in other words, a small irreversible change in an isolated system is always subject to the condition that there is an increase of entropy

It may perhaps be useful to explain here a difficulty which is sometimes expressed, viz that if a change in entropy is defined as $\frac{dQ}{\theta}$ or its integral, then for any change in which dQ is zero the change in entropy should be zero The point to be remembered is that the change in entropy on passing from A to B is defined as $\int \frac{dQ}{\theta}$ for any one of the possible *reversible* paths connecting A and B When we say that the system passes irreversibly from A to B, there being no heat absorbed or given out, and the entropy increasing, it means that A and B stand in such a relation to one another that although an irreversible process for which $dQ=0$ may connect them, any *reversible* process connecting them could not have a zero value for dQ

CONDITIONS OF THERMODYNAMIC EQUILIBRIUM

The criterion of thermodynamic equilibrium is the following If the system is in such a state that a small displacement is a reversible one, then it is in equilibrium This requires some elucidation It follows from the considerations given at the end of Chapter III The condition that the change shall be a reversible one is that in respect of all mechanical constraints driving and opposing forces shall be equal, while heat exchanges must be made with reservoirs differing infinitely little in temperature This condition naturally implies that the system is in a state of equilibrium—the reversible change is nothing more than the continuous adjustment of infinitesimal displacements from equilibrium, in Duhem's phrase, 'une suite continue d'états d'équilibre' The above criterion is analogous, therefore, to the principle of virtual work in mechanics

Now we have already a criterion for the reversibility of a given modification in the state of a system, if $\frac{dQ}{\theta}=dS$, then the change is reversible, while, if $\theta dS=dQ+\Delta$, then the change is not reversible The condition for equilibrium, therefore, is that for a small displacement θdS shall be equal to dQ In particular, the condition that a system shall be in equilibrium is that for a small *adiabatic* displacement dS shall be zero

The application of this result yields a great many thermodynamic relationships much more simply and easily than they can be obtained by cyclic processes.

We may, as a first example, apply it to the problem of chemical equilibrium To lend precision to our ideas we will consider the specific reaction

$$2H_2+O_2 \rightleftharpoons 2H_2O+U \text{ calories}$$

Let the respective concentrations of hydrogen, oxygen, and water, which are in equilibrium in a system at temperature θ be C_{H_2}, C_{O_2}, C_{H_2O}, expressed in gram molecules per litre.

Let the system undergo a small virtual change such that $2dn$ molecules of water are formed, the temperature remaining constant Udn calories are liberated and must be removed from the system

The condition that the system is in equilibrium is that the change in entropy accompanying the virtual change shall be equal to $\frac{dQ}{\theta}$, which in this case becomes $-\frac{Udn}{\theta}$ (Q being heat absorbed, U heat liberated)

The change in entropy accompanying the virtual change can be calculated as follows Entropy is a property such that the entropy of two gram molecules is twice as great as the entropy of one In the change $2dn$ gram molecules of water appear while dn gram molecules of oxygen and $2dn$ of hydrogen disappear The total change in entropy of the system is thus entropy of $2dn$ gram molecules of water—entropy of $2dn$ gram molecules of hydrogen—entropy of dn gram molecules of oxygen.

Using the expression for the entropy of a perfect gas, namely

$$S=C_v \ln \theta-R \ln C+k,$$

we have for the change under consideration,

$$\begin{aligned} dS&=2dn\,\{C_{vH_2O} \ln \theta-R \ln C_{H_2O}+k_{H_2O}\}-2dn\,\{C_{vH_2} \ln \theta \\ &\quad -R \ln C_{H_2}+k_{H_2}\}-dn\,\{C_{vO_2} \ln \theta-R \ln C_{O_2}+k_{O_2}\} \\ &=dn\,\{2k_{H_2O}-2k_{H_2}-k_{O_2}\}+dn\,\{2C_{vH_2O}-2C_{vH_2}-C_{vO_2}\} \ln \theta \\ &\quad +dn \quad R \ln \frac{C^2_{H_2} \cdot C_{O_2}}{C^2_{H_2O}}. \end{aligned}$$

The condition for equilibrium gives

$$dS=-\frac{Udn}{\theta}$$

Therefore

$$-\frac{Udn}{\theta}=dn\left\{2k_{H_2O}-2k_{H_2}-k_{O_2}\right\}+dn\left\{2C_{vH_2O}-2C_{vH_2}-C_{vO_2}\right\}\ln \theta$$
$$+dn \quad R \ln \frac{C^2_{H_2} \; C_{O_2}}{C^2_{H_2O}}$$

U, k_1, C_v, and R are all independent of the concentration, so that, provided θ is constant, $\frac{C^2_{H_2O} \; C_{O_2}}{C^2_{H_2O}}$ is constant

Thus $$-\frac{U}{\theta}=\Sigma k+\left\{2C_{vH_2O}-2C_{vH_2}-C_{vO_2}\right\} \ln \theta+R \ln K$$

Differentiating with respect to temperature, and treating the specific heats as constant, we have

$$\frac{U}{\theta^2}-\frac{1}{\theta}\frac{dU}{d\theta}=\left\{2C_{vH_2O}-2C_{vH_2}-C_{vO_2}\right\}\frac{1}{\theta}+R\frac{d\ ln\ K}{d\theta}$$

But since
$$\frac{dU}{d\theta}=2C_{vH_2}+C_{vO_2}-2C_{vH_2O},$$

$$\frac{U}{\theta^2}=R\frac{d\ ln\ K}{d\theta},$$

or
$$\frac{d\ ln\ K}{d\theta}=\frac{U}{R\theta^2}$$

This method is rather simpler than that depending upon the van't Hoff equilibrium box

As a second example, we may derive the usual formula for the electromotive force of a concentration cell Let the cell consist of silver electrodes in silver nitrate solutions of concentration C_1 and C_2, which are both small enough for the salt to be nearly completely ionised Let dx Faradays of electricity flow through the cell The electrical work done by the cell is $Edx\times 96540$ volt-coulombs In calories this is $Edx\times 96540\times 0{\cdot}24$. As explained in an earlier section this energy is derived entirely from the heat of the surroundings We suppose the temperature to remain constant The cell thus absorbs q calories

The net result of its working is that for every Faraday which has passed $(1-n)$ gram molecules of ionised silver nitrate are transferred from the strong to the weak solution,* where n is transport number of the silver ion Each molecule consists of two independent ions Thus $2(1-n)$ particles are transferred for each Faraday or $2(1-n)dx$ in all

The increase in entropy when this number of gram-particles pass from concentration C_1 to concentration C_2 is

$$2(1-n)dx(C_v\ ln\ \theta-R\ ln\ C_2)-2(1-n)dx(C_v\ ln\ \theta-R\ ln\ C_1)$$
$$=2(1-n)dxR\ .\ ln\ \frac{C_1}{C_2}.$$

For equilibrium, and there is only equilibrium when E is the true electromotive force, this change in entropy is $\frac{q}{\theta}$

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* The silver electrode in the weaker solution is the negative pole and dissolves when the cell works For each Faraday which passes 1 gram ion of silver dissolves into the weaker solution, but n gram ions migrate into the strong solution The gain is thus $(1-n)$ gram ions of silver These, together with the $(1-n)$ grams ions of NO_3 which enter the weaker solution by migration, make up the $(1-n)$ gram molecules of silver nitrate In exactly the same way it may be seen that the stronger solution loses $(1-n)$ gram molecules of silver nitrate

Thus $$\frac{q}{\theta}=\frac{Edx\times 96540\times 0\cdot 24}{\theta}=2(1-n)dx\ R\ \ ln\frac{C_1}{C_2},$$

$$E=\frac{2R\theta(1-n)}{96540\times 0\cdot 24}\ ln\frac{C_1}{C_2}$$

Since n is not very different from 0·5 this reduces to

$$E=\frac{R\theta}{96540\times 0\cdot 24}\ ln\frac{C_1}{C_2}$$

FREE ENERGY AND THERMODYNAMIC POTENTIAL

We have hitherto made use of the equation $Q=A-U$, Q being heat absorbed, A external work performed, and U the decrease in internal energy This is, of course, true for any change, whether finite or infinitesimal In order to combine it, however, with the equilibrium condition $dQ=\theta dS$, it will be convenient to re-write it in a differential form For this purpose we introduce a symbol $\mathbf{U}$ for the internal energy of the system, a quantity which is of course indeterminate, since we only deal with changes in it If the system passes from state 1 to state 2, we have $\mathbf{U}_1-\mathbf{U}_2=U$.

U is the *decrease* in $\mathbf{U}$, therefore, in the differential form, we replace U by $-d\mathbf{U}$

Further, the work done by the system may be represented by the sum of two terms, one, pdv, being that done against the external pressure p, and dW being work of any other description

We thus have the two fundamental equations

$$dQ=pdv+dW+d\mathbf{U},$$
$$dQ=\theta dS$$

Combining these, we have

$$d\mathbf{U}+pdv-\theta dS+dW=0$$

This equation applies to all reversible changes, and only to these It is thus the general condition of equilibrium It is quite general in the sense that the small displacements to which it refers are not restricted to isothermal, or adiabatic displacements, or constant volume, or constant pressure changes

It is often convenient, however, when investigating the equilibrium of a system to consider a small virtual change subject to some special condition The equation then assumes simpler forms

(a) *Adiabatic changes*

$\theta dS = 0$, as we have already seen

(b) *Isothermal changes*

In this case $d\theta = 0$

We may therefore replace θdS by $d(\theta S)$, since this in general is $\theta dS + S d\theta$

Therefore the condition of equilibrium becomes

$$d(U - \theta S) + p dv + dW = 0$$

(c) *Changes at constant temperature and constant volume*

$$d\theta = 0, \quad dv = 0$$

Therefore the condition of equilibrium reduces still further to

$$d(U - \theta S) + dW = 0$$

(d) *Changes at constant temperature and constant pressure*

$$d\theta = 0, \quad dp = 0$$

$p dv$ can now be replaced by $d(pv)$, since $d(pv) = p dv + v dp$, and $v dp = 0$

Therefore the condition of equilibrium becomes

$$d(U - \theta S + pv) + dW = 0$$

Let us consider (c) and (d) more closely Owing to the restricting conditions we are enabled to collect under one differential sign $U - \theta S$ in one case, and $U - \theta S + pv$ in the other These are quite ordinary properties of the system like U itself We may therefore write

$$U - \theta S = F, \quad d(U - \theta S) = dF,$$
$$U - \theta S + pv = \varphi, \quad d(U - \theta S + pv) = d\varphi$$

The equilibrium relationships can be written thus

(i) $\theta dS = 0$ for a virtual adiabatic change
(ii) $dF + p dv + dW = 0$ for an isothermal change
(iii) $dF + dW = 0$ for a virtual change at constant temperature and volume
(iv) $d\varphi + dW = 0$ for a virtual change at constant temperature and pressure

The relation $\theta dS = 0$ means that S is a maximum or minimum when the system is in equilibrium We have already seen that S increases in irreversible changes, i e spontaneous changes towards equilibrium Thus, S is a maximum when the system is in equilibrium

Since $F = U - \theta S$, and $\varphi = U - \theta S + pv$, it appears that *increases* in entropy correspond to *decreases* in F and φ

Let us consider for the moment the case when $dW = 0$ The equilibrium condition is now that for changes at constant pressure and temperature $d\varphi = 0$, and for changes at constant volume and temperature $dF=0$ Thus, F and φ have minimum values, since we have just seen that they tend always to decrease rather than increase

φ is called the thermodynamic potential of the system F is sometimes called the Free Energy—though there is a certain amount of latitude about the use of this term, and it is always necessary to find out what different writers mean by it

When dW is not zero,

$$dF+dW=0 \text{ for changes at constant volume and temperature,}$$

therefore $dW=-dF$.

The decrease in F gives the external work done

Similarly, for changes at constant pressure and temperature,

$$dW=-d\varphi$$

The decrease in thermodynamic potential gives the external work other than that done against the pressure

For any isothermal change

$$-dF=pdv+dW$$

The decrease in F gives the total work done

An alternative form of constant temperature and pressure condition is used by Planck, which we will introduce later in dealing with a special example of its application

By the employment of the thermodynamic functions, φ or F, many calculations can be put into a concise and convenient form We have already derived the law of mass action by means of the van't Hoff equilibrium box, and by entropy considerations It will perhaps be instructive to make the same calculation with the aid of the function F, although it is, of course, the original calculation thrown into a new form Later we shall see how the lowering of freezing point of dilute solutions can be conveniently treated with the aid of a thermodynamic function

CHEMICAL EQUILIBRIUM IN GASES TREATED WITH THE AID OF F

As before we may take the reaction

$$2H_2+O_2\rightleftharpoons 2H_2O+U \text{ calories,}$$

U being the heat of reaction at constant volume

The concentrations are C_{H_2}, C_{O_2}, C_{H_2O} respectively at equilibrium, the temperature being θ

Let there be a small displacement from equilibrium at constant temperature and volume such that $2dn$ gram molecules of water are formed at the expense of $2dn$ of hydrogen and dn of oxygen

Since the change is a virtual change from equilibrium, $dF=O$.

$$\text{Now } dF=2F_{H_2O}dn-2F_{H_2}dn-F_{O_2}dn \text{ *}$$

$$F_{H_2O}=\mathbf{U}_{H_2O}-\theta S_{H_2O}=\mathbf{U}_{H_2O}-\theta C_{vH_2O}\,ln\,\theta+R\theta\,ln\,C_{H_2O}-\theta k_{H_2O},$$

and similarly for F_{H_2} and F_{O_2}

Thus the equilibrium condition is

$$dF=(2\mathbf{U}_{H_2O}-2\mathbf{U}_{H_2}-\mathbf{U}_{O_2})dn-\theta\,ln\,\theta(2C_{vH_2O}-2C_{vH_2}-C_{vO_2})dn$$
$$+R\theta\,ln\,\frac{C^2_{H_2O}}{C^2_{H_2}C_{O_2}}dn-\theta(2k_{H_2O}-2k_{H_2}-k_{O_2})dn=0$$

$2\mathbf{U}_{H_2O}-2\mathbf{U}_{H_2}-\mathbf{U}_{O_2}$ is the excess of the internal energy of two gram molecules of steam over the sum of the internal energies of two molecules of hydrogen and one of oxygen It is thus the heat absorbed in the formation of water or $-U$ of the chemical equation

Thus

$$-U-\theta\,ln\,\theta(2C_{vH_2O}-2C_{vH_2}-C_{vO_2})+R\theta\,ln\,\frac{C^2_{H_2O}}{C^2_{H_2}C_{O_2}}$$
$$-\theta(2k_{H_2O}-2k_{H_2}-k_{O_2})=0$$

This is the equation we obtained before

From it $\frac{C^2_{H_2O}}{C^2_{H_2}C_{O_2}}$ is seen to be a constant at constant temperature By differentiation the equation connecting equilibrium constant and temperature is found as before

This method, of course gives us,

$$\frac{d\,ln\,K_v}{d\theta}=\frac{U_v}{R\theta^2}$$

We could equally well have made the calculation using the

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* It is perhaps useful to point out that if we have l, m, and n molecules respectively of steam, hydrogen, and oxygen, F, the total value of the function for the system, is given by

$$F=lF_{H_2O}+mF_{H_2}+nF_{O_2},$$

where F_{H_2O} is the value for one gram molecule of steam, and so on

When the virtual change takes place at constant temperature and volume, l, m, and n are the only variables We may write

$$dF=F_{H_2O}dl+ldF_{H_2O}+F_{H_2}dm+mdF_{H_2}+F_{O_2}dn+ndF_{O_2}$$

But in the virtual displacement considered the values of F_{H_2O}, etc, which refer to gram molecules of each of the substances, do not change The changes in the total value of F for the system are accounted for by the variations dl, dm, dn Since for $2dn$ gram molecules of water to be formed $dl=2dn$, $dm=-2dn$, $dn=-dn$, we arrive at the above equation function φ, and making the virtual displacement at constant pressure We should then find

$$\frac{d \ln K_p}{d\theta} = \frac{U_p}{R\theta^2}$$

PARTIAL DIFFERENTIAL RELATIONSHIPS OF THERMODYNAMIC QUANTITIES INTRODUCTORY NOTE

Certain partial differential relationships of the thermodynamic functions are often of great importance, so that a brief discussion of them will now be given

Most of the properties of a system are interdependent, and one property can usually be expressed in terms of several others, or, in other words, it is a function of the others Thus the volume of a given mass of gas is a function of the temperature and pressure e g ,

$$v = \frac{R\theta}{p}$$

If we wish to find how the volume varies with temperature while pressure is kept constant we differentiate partially with respect to θ, thus

$$\frac{\partial v}{\partial \theta} = \frac{R}{p},$$

or, if we wish to find how the volume varies with the pressure when the temperature is kept constant we differentiate partially with respect to p, thus

$$\frac{\partial v}{\partial p} = \frac{-R\theta}{p^2}$$

If the volume were changing with regard to yet another variable, say time, we should have

$$\frac{dv}{dt} = \frac{\partial v}{\partial \theta}\frac{d\theta}{dt} + \frac{\partial v}{\partial p}\frac{dp}{dt}.$$

In general if a quantity u is a function of the variables x, y, z

$$u = f(x, y, z \qquad)$$

then $$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy + \frac{\partial u}{\partial z}dz$$

This is one result which is very frequently used

Another important property of partial differentials is that known as the commutative property. If

$$u=f(x, y),$$

then
$$\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right)=\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right),$$

provided that u is a finite, continuous and single-valued function of x and y It would not, for example, be permissible to apply this theorem to a quantity such as dQ since there is no quantity Q which depends simply upon the properties of the system Q is entirely dependent upon arbitrarily prescribed paths by which systems undergo their changes dQ is not a complete differential The proof of the commutative relation is as follows

u depends only on x and y

Let x change to $x+dx$ and y to $y+dy$ The new value of u is $u+du$

We may think of the change as occurring in two ways first, x remains constant while y increases to $y+dy$, and then x changes while y remains constant Secondly, we may let the change in x take place first and the change in y subsequently In either case du must have the same value In the first case we have y changes to $y+dy$, u thereby becomes $u+\frac{\partial u}{\partial y}dy$ x now increases by dx, the final value of u is

$$u+\frac{\partial u}{\partial y}dy+\frac{\partial}{\partial x}\left(u+\frac{\partial u}{\partial y}dy\right)dx$$

Similarly when we let x increase first we find for the final value of u the expression

$$u+\frac{\partial u}{\partial x}dx+\frac{\partial}{\partial y}\left(u+\frac{\partial u}{\partial x}dx\right)dy$$

Equating this to the previously obtained value and cancelling terms common to both we find

$$\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right)dxdy=\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right)dxdy$$

The commutative relation is thus proved

APPLICATIONS

For a system in which the only external work which is done is against an external pressure we have seen that the fundamental equations hold,

$$dQ=d\boldsymbol{U}+pdv,$$
$$dQ=\theta dS,$$
$$d\boldsymbol{U}+pdv-\theta dS=0$$

These can be transformed in various ways, thus

$$dF=d(\boldsymbol{U}-\theta S)=-Sd\theta-pdv \tag{1}$$

For $d(\boldsymbol{U}-\theta S)=d\boldsymbol{U}-\theta dS-Sd\theta,$

but $d\boldsymbol{U}-\theta dS=-pdv,$

whence (1) follows

Similarly

$$d\varphi=d(\boldsymbol{U}-\theta S+pv)=vdp-Sd\theta \tag{2}$$
$$d\boldsymbol{U}=\theta dS-pdv \tag{3}$$
$$d(\boldsymbol{U}+pv)=\theta dS+vdp \tag{4}$$

Consider the first of these equations,

$$dF=-Sd\theta-pdv \tag{1}$$

We are at liberty to express F in a general manner as a function of θ and v, thus

$$F=f(\theta\, v),$$

and then to write

$$dF=\frac{\partial F}{\partial \theta}d\theta+\frac{\partial F}{\partial v}dv$$

Comparing this with (1) it will be seen that

$$\frac{\partial F}{\partial \theta}=-S \text{ and } \frac{\partial F}{\partial v}=-p$$

Now since $$\frac{\partial}{\partial v}\left(\frac{\partial F}{\partial \theta}\right)=\frac{\partial}{\partial \theta}\left(\frac{\partial F}{\partial v}\right),$$

$$-\frac{\partial S}{\partial v}=-\frac{\partial p}{\partial \theta},$$

or $$\frac{\partial S}{\partial v}=\frac{\partial p}{\partial \theta}$$

In order to make quite clear that, in the operation of differentiating S partially with respect to v, the other variable which is kept constant is θ, and vice versa it is usual to write

$$\left(\frac{\partial S}{\partial v}\right)_\theta=\left(\frac{\partial p}{\partial \theta}\right)_v$$

Other analogous relationships may be obtained similarly

The method of calculation here employed should be carefully noted The fundamental equation $dU+pdv-\theta dS=0$ is written down, and put into such a form by transposition or addition of terms to each side that the left hand side becomes a complete differential, and two differential terms remain on the right hand side as in the several equations (1) to (4) The quantity whose differential appears on the left hand side is now expressed in a formal manner as a function of the two quantities whose differentials appear on the right The new equation is differentiated, in the form $du=\frac{\partial u}{\partial x}dx+\frac{\partial u}{\partial y}dy$, and the result is compared with the first equation The values of the partial differential coefficients are read off and the commutative relation is applied The procedure may be exemplified by deriving the three well-known thermodynamic relations

$$\left(\frac{\partial\theta}{\partial v}\right)_s=-\left(\frac{\partial p}{\partial S}\right)_v$$

$$\left(\frac{\partial\theta}{\partial p}\right)_s=\left(\frac{\partial v}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial p}\right)_\theta=-\left(\frac{\partial v}{\partial\theta}\right)_p$$

In the first of these the 'independent variables' are S and v

They are called independent variables because we are at liberty to vary them one at a time in any way we please. Now in accordance with the directions given above we express the general equation in such a way that a complete differential appears on the left and two differentials on the right Moreover we must select for the two differentials which appear on the right those of the two independent variables, in this case S and v Equation (3) above gives the appropriate form

$$dU=\theta dS-pdv$$

Now we write

$$U=f(S,v),$$

$$dU=\frac{\partial U}{\partial S}dS+\frac{\partial U}{\partial v}dv$$

By comparing the two forms of the expression for dU we see

$$\frac{\partial U}{\partial S}=\theta \text{ and } \frac{\partial U}{\partial v}=-p,$$

and since
$$\frac{\partial}{\partial v}\left(\frac{\partial \boldsymbol{U}}{\partial S}\right)=\frac{\partial}{\partial S}\left(\frac{\partial \boldsymbol{U}}{\partial v}\right),$$
$$\left(\frac{\partial \theta}{\partial v}\right)_s=-\left(\frac{\partial p}{\partial S}\right)_v$$

In order to obtain the relation $\left(\frac{\partial \theta}{\partial p}\right)_s=\left(\frac{\partial v}{\partial S}\right)_p$ we need the differentials dS and dp on the right hand side We therefore transpose the fundamental equation thus
$$d(\boldsymbol{U}+pv)=\theta dS+vdp,$$
whence
$$\frac{\partial(\boldsymbol{U}+pv)}{\partial S}=\theta \text{ and } \frac{\partial(\boldsymbol{U}+pv)}{\partial p}=v$$

Therefore
$$\left(\frac{\partial \theta}{\partial p}\right)_s=\left(\frac{\partial v}{\partial S}\right)_p$$

The derivation of the remaining relation is as follows
$$d(\boldsymbol{U}-\theta S+pv)=d\varphi=vdp-Sd\theta,$$
therefore
$$\frac{\partial \varphi}{\partial p}=v \text{ and } \frac{\partial \varphi}{\partial \theta}=-S,$$
thus
$$\left(\frac{\partial v}{\partial \theta}\right)_p=-\left(\frac{\partial S}{\partial p}\right)_\theta$$

Suppose now that we require a relation of this sort with p and v as the independent variables It will be seen by trial that by no sort of rearrangement of the fundamental equation can we obtain an expression with dp and dv only on one side and a complete differential on the other. We therefore proceed thus
$$d\boldsymbol{U}=\theta dS-pdv.$$

Replace dS by its equivalent $\frac{\partial S}{\partial p}dp+\frac{\partial S}{\partial v}dv$

Then
$$d\boldsymbol{U}=\theta\frac{\partial S}{\partial p}dp+\theta\frac{\partial S}{\partial v}dv-pdv,$$
$$=\theta\frac{\partial S}{dp}dp+\left(\theta\frac{\partial S}{\partial v}-p\right)dv$$

We now have an expression of the required form,

but
$$d\boldsymbol{U}=\frac{\partial \boldsymbol{U}}{\partial p}dp+\frac{\partial \boldsymbol{U}}{\partial v}dv,$$

therefore $$\frac{\partial U}{\partial p}=\theta\frac{\partial S}{\partial p} \text{ and } \frac{\partial U}{\partial v}=\theta\frac{\partial S}{\partial v}-p,$$

and since $$\frac{\partial}{\partial v}\left(\frac{\partial U}{\partial p}\right)=\frac{\partial}{\partial p}\left(\frac{\partial U}{\partial v}\right),$$

$$\frac{\partial}{\partial v}\left(\theta\frac{\partial S}{\partial p}\right)=\frac{\partial}{\partial p}\left(\theta\frac{\partial S}{\partial v}-p\right),$$

$$\frac{\partial\theta}{\partial v}\frac{\partial S}{\partial p}+\theta\frac{\partial}{\partial v}\left(\frac{\partial S}{\partial p}\right)=\frac{\partial\theta}{\partial p}\frac{\partial S}{\partial v}+\theta\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial v}\right)-\frac{\partial p}{\partial p},$$

but $$\frac{\partial}{\partial v}\left(\frac{\partial S}{\partial p}\right)=\frac{\partial}{\partial p}\left(\frac{\partial S}{\partial v}\right) \text{ and } \frac{\partial p}{\partial p}=1,$$

therefore $$\left(\frac{\partial\theta}{\partial v}\right)_p\left(\frac{\partial S}{\partial p}\right)_v=\left(\frac{\partial\theta}{\partial p}\right)_v\left(\frac{\partial S}{\partial v}\right)_p-1,$$

or $$\left(\frac{\partial S}{\partial v}\right)_p\left(\frac{\partial\theta}{\partial p}\right)_v-\left(\frac{\partial S}{\partial p}\right)_v\left(\frac{\partial\theta}{\partial v}\right)_p=1$$

The importance of these partial differential relationships is twofold In the first place they are often important in themselves They correlate various properties, giving quantities which are difficult to determine directly in terms of others which are easily determinable by experiment But secondly the partial differential coefficients of the free energy and of the thermodynamic potential are useful in determining the variation of equilibrium conditions with temperature, pressure and so on

Some examples follow, in which the method of working should be carefully noted

TO SHOW THAT FOR ANY SUBSTANCE THE DIFFERENCE BETWEEN THE TWO SPECIFIC HEATS IS GIVEN BY

$$C_p-C_v=\theta\left(\frac{\partial v}{\partial\theta}\right)_p\left(\frac{\partial p}{\partial\theta}\right)_v,$$

$$C_p=\left(\frac{\partial Q}{\partial\theta}\right)_p, \quad C_v=\left(\frac{\partial Q}{\partial\theta}\right)_v$$

These differentials, however, are inconvenient, being derived from Q of which dQ is not a complete differential.

We replace $\frac{\partial Q}{\partial \theta}$ therefore by $\theta\frac{\partial S}{\partial \theta}$ and we have

$$C_p-C_v=\theta\left\{\left(\frac{\partial S}{\partial \theta}\right)_p-\left(\frac{\partial S}{\partial \theta}\right)_v\right\},$$

$$=\theta\left(\frac{\partial v}{\partial \theta}\right)_p\left(\frac{\partial p}{\partial \theta}\right)_v\frac{\left\{\left(\frac{\partial S}{\partial \theta}\right)_p-\left(\frac{\partial S}{\partial \theta}\right)_v\right\}}{\left(\frac{\partial v}{\partial \theta}\right)_p\left(\frac{\partial p}{\partial \theta}\right)_v},$$

$$=\theta\left(\frac{\partial v}{\partial \theta}\right)_p\left(\frac{\partial p}{\partial \theta}\right)_v\left\{\left(\frac{\partial S}{\partial \theta}\right)_p\left(\frac{\partial \theta}{\partial v}\right)_p\left(\frac{\partial \theta}{\partial p}\right)_v-\left(\frac{\partial S}{\partial \theta}\right)_v\left(\frac{\partial \theta}{\partial p}\right)_v\left(\frac{\partial \theta}{\partial v}\right)_p\right\},$$

for, provided that the subscript is kept the same, $\frac{1}{\frac{\partial v}{\partial \theta}}=\frac{\partial \theta}{\partial v}$

Moreover, still provided that the subscript is the same,

$$\left(\frac{\partial S}{\partial \theta}\right)_p\left(\frac{\partial \theta}{\partial v}\right)_p=\left(\frac{\partial S}{\partial v}\right)_p,$$

though we could not combine, say, $\left(\frac{\partial S}{\partial \theta}\right)_p\left(\frac{\partial \theta}{\partial v}\right)_S$ in this way

Therefore

$$C_p-C_v=\theta\left(\frac{\partial v}{\partial \theta}\right)_p\left(\frac{\partial p}{\partial \theta}\right)_v\left\{\left(\frac{\partial S}{\partial v}\right)_p\left(\frac{\partial \theta}{\partial p}\right)_v-\left(\frac{\partial S}{\partial p}\right)_v\left(\frac{\partial \theta}{\partial v}\right)_p\right\}.$$

The expression in brackets was found to be equal to unity on page 128 This yields the desired result

$$C_p-C_v=\theta\left(\frac{\partial v}{\partial \theta}\right)_p\left(\frac{\partial p}{\partial \theta}\right)_v.$$

RELATION BETWEEN THE COEFFICIENTS OF EXPANSION, COMPRESSIBILITY AND INCREASE OF PRESSURE WITH TEMPERATURE FOR ANY SUBSTANCE

$$v=f(p,\theta)$$

$$dv=\left(\frac{\partial v}{\partial p}\right)_\theta dp+\left(\frac{\partial v}{\partial \theta}\right)_p d\theta$$

If $dv=0$, that is for a change at constant volume,

$$\left(\frac{\partial v}{\partial p}\right)_\theta dp+\left(\frac{\partial v}{\partial \theta}\right)_p d\theta=0$$

Therefore
$$-\frac{\left(\frac{\partial v}{\partial p}\right)_\theta}{\left(\frac{\partial v}{\partial \theta}\right)_p}=\frac{d\theta}{dp}.$$

Now $\frac{d\theta}{dp}$ subject to the condition that $dv=0$ is $\left(\frac{\partial \theta}{\partial p}\right)_v$

Therefore
$$-\frac{\left(\frac{\partial v}{\partial p}\right)_\theta}{\left(\frac{\partial v}{\partial \theta}\right)_p}=\left(\frac{\partial \theta}{\partial p}\right)_v,$$

or
$$\left(\frac{\partial p}{\partial \theta}\right)_v=-\frac{\left(\frac{\partial v}{\partial \theta}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_\theta}$$

Combining this last relation with the equation

$$C_p-C_v=\theta\left(\frac{\partial v}{\partial \theta}\right)_p\left(\frac{\partial p}{\partial \theta}\right)_v$$

we find
$$C_p-C_v=-\theta\left(\frac{\partial v}{\partial \theta}\right)_p^2\left(\frac{\partial p}{\partial v}\right)_\theta$$

If v_0=the volume of one gram or one gram molecule of the substance, according as C_p and C_v are gram or molecular specific heats, α=coefficient of cubical expansion$=\frac{1}{v_0}\left(\frac{\partial v}{\partial \theta}\right)_p$

Note that the coefficient of cubical expansion is not $\frac{\partial v}{\partial \theta}$ but $\frac{1}{v_0}\frac{\partial v}{\partial \theta}$, that is increase in volume per unit of original volume

$\varkappa$=coefficient of compressibility $=-\frac{1}{v_0}\left(\frac{\partial v}{\partial p}\right)_\theta$

This is negative, since the volume decreases with increase of pressure

Thus $$C_p - C_v = \frac{\theta \alpha^2 v_0}{\gamma}$$

This relation is frequently employed—since α and γ are quantities which have been carefully determined for a great many substances C_v for solids and liquids is difficult to find directly

CHANGE OF STATE AN ILLUSTRATION OF THE RELATION

$$\left(\frac{\partial S}{\partial v}\right)_\theta = \left(\frac{\partial p}{\partial \theta}\right)_v.$$

Let v_1 and v_2 be the specific volumes of two co-existent phases, and let a quantity dm of substance change its state at constant temperature θ

Then if the latent heat be l calories per gram, the heat absorbed is given by the equation

$$dQ = \theta dS = l dm$$

If the volume change is dv, then

$$(v_2 - v_1) dm = dv$$

Therefore $$dS = \frac{l dm}{\theta} = \frac{l dv}{\theta(v_2 - v_1)}$$

This is at constant temperature, we may therefore write

$$\left(\frac{\partial S}{\partial v}\right)_\theta = \frac{l}{(v_2 - v_1)\theta},$$

but $$\left(\frac{\partial S}{\partial v}\right)_\theta = \left(\frac{\partial p}{\partial \theta}\right)_v \qquad \left(\frac{\partial p}{\partial \theta}\right)_v = \frac{l}{(v_2 - v_1)\theta}$$

FURTHER ILLUSTRATIONS PLANCK'S TREATMENT OF DILUTE SOLUTIONS

PLANCK'S POTENTIAL. As we have seen, since $dU + pdv = dQ = \theta dS$, we have

$$\theta dS - dU - d(pv) = -vdp,$$

$$dS - \frac{(dU + pv)}{\theta} = -\frac{vdp}{\theta},$$

and if θ is constant,

$$d\left(S - \frac{U + pv}{\theta}\right) = -\frac{vdp}{\theta}$$

When, further, pressure is also constant the relation

$$d\left(S-\frac{U+pv}{\theta}\right)=0$$

holds good for a reversible change, and this is the condition of equilibrium for a system which is subject only to an external pressure

The quantity $S-\frac{U+pv}{\theta}$ is sometimes called Planck's potential We may denote it by Φ Φ, although a quantity which was originally defined with reference to changes at constant temperature and pressure, has of course different values at different temperatures and different pressures The way in which Φ varies with temperature is seen by differentiating partially with respect to θ Thus

$$\left(\frac{\partial\Phi}{\partial\theta}\right)_p=\frac{\partial S}{\partial\theta}-\frac{1}{\theta}\frac{\partial}{\partial\theta}(U+pv)+\frac{U+pv}{\theta^2},$$

$$=\frac{\partial S}{\partial\theta}-\frac{1}{\theta}\left(\frac{\partial U}{\partial\theta}+p\frac{\partial v}{\partial\theta}\right)+\frac{U+pv}{\theta^2},$$

p being constant

Since from the fundamental equation $dS=\frac{1}{\theta}(dU+pdv)$,

$$\frac{\partial S}{\partial\theta}-\frac{1}{\theta}\left(\frac{\partial U}{\partial\theta}+p\frac{\partial v}{\partial\theta}\right)=0$$

Hence
$$\left(\frac{\partial\Phi}{\partial\theta}\right)_p=\frac{U+pv}{\theta^2},$$

a relation which will be needed, as we shall presently show how freezing point lowering may be discussed with its aid

POTENTIAL OF A MIXTURE OF PERFECT GASES

We first need the value of Φ for a mixture of perfect gases

We have
$$\Phi=\Sigma n\left[S-\frac{U+pv}{\theta}\right]$$

But from the result on page 113 S for each gram molecule in the mixture

$$=C_v\,ln\,\theta+R\,ln\,v-R\,ln\,x,$$

where x is the fractional molecular concentration of the given gas, thus,

$$\Phi=\Sigma n\left[C_v \ln \theta+R \ln v-R \ln x\right]-\Sigma n\left(\frac{U+pv}{\theta}\right)$$

The only terms here depending on the *concentration* of the gases are the x terms Hence, collecting together the other terms, which are dependent only on the nature of the gas, the temperature, and the *total* pressure—not the separate partial pressures—we may write

$$\Phi=\Sigma n(\varphi-R \ln x)$$

φ being a symbol for the terms independent of concentration

DILUTE SOLUTIONS

Let n_0 be the number of gram molecules of solvent, n_1, n_2, etc , the number of gram molecules of the various dissolved substances

The total volume V of the dilute solution is given by

$$V=n_0v_0+n_1v_1+n_2v_2$$

where v_1, v_2, etc , depend upon the solvent as well as the solute, but are not influenced by the mutual interaction of the solutes or of the molecules of a given solute among themselves

Similarly U the energy is given by

$$U=n_0u_0+n_1u_1+n_2u_2$$

To get the entropy we have by definition of entropy the differential relation,

$$dS=\frac{dU+pdV}{\theta}=n_0\frac{du_0+pdv_0}{\theta}+n_1\frac{du_1+pdv_1}{\theta}$$

Since u_0, u_1, u_2, etc , and v_0, v_1, v_2, etc , are independent of n_0, n_1, etc , and only dependent on p and θ, we can write

$$ds_0=\frac{du_0+pdv_0}{\theta},\quad ds_1=\frac{du_1+pdv_1}{\theta}\text{ etc.}$$

Thus $$dS=n_0ds_0+n_1ds_1+n_2ds_2$$

$$S=n_0s_0+n_1s_1+n_2s_2\ .\ .\ .\ +C$$

The integration constant may depend on n_0, n_1, n_2 . though by its nature as an integration constant it is independent of p and θ

Planck evaluates it by the following device

Imagine the temperature to be increased, and the pressure decreased till the whole system passes into the state of a perfect gas, the entropy of which is given by

$$\begin{aligned} S=&n_0[C_{v_0}\, ln\ \theta+R\, ln\ v-R\, ln\ x_0] \\ &+n_1[C_{v_1}\, ln\ \theta+R\, ln\ v-R\, ln\ x_1] \\ &+n_2[\qquad] \end{aligned}$$

where $\quad x_0$ as before $=\dfrac{n_0}{n_0+n_1+n_2}$ etc

These two expressions for S must be identical Hence the only terms which are independent of pressure and temperature must be equal in the two cases

Thus $\quad C=-[n_0R\, ln\ x_0+n_1R\, ln\ x_1+n_2R\, ln\ x_2 \qquad]$

Thus $\quad S=\Sigma n[s-R\, ln\ x]$

Whence $\quad \Phi=S-\dfrac{U+pV}{\theta}$.

$$=\Sigma n\left(s-R\ ln\ x-\frac{u+pv}{\theta}\right)$$

Collecting up the terms independent of x by putting

$$s_0-\frac{u_0+p_0v_0}{\theta}=\varphi_0, \text{ etc },$$

we arrive at the expression

$$\Phi=\Sigma n(\varphi-R\, ln\ x),$$

that is,

$$n_0(\varphi_0-R\, ln\ x_0)+n_1(\varphi_1-R\, ln\ x_1)+n_2(\varphi_2-R\, ln\ x_2)$$

EQUILIBRIUM BETWEEN A SOLID SOLVENT AND A SOLUTION LOWERING OF FREEZING POINT

Let n_1 molecules of a solute be dissolved in n_0 of a solvent, then $x_0=\dfrac{n_0}{n_0+n_1}$ and $x_1=\dfrac{n_1}{n_0+n_1}$, and Φ, the Planck potential of the solution, is given by

$$\Phi=\underset{\text{solvent}}{n_0(\varphi_0-R\, ln\ x_0)}+\underset{\text{solute}}{n_1(\varphi_1-R\, ln\ x_1)}$$

Suppose the solution to be at its freezing point Then solvent can separate reversibly It can do this at the freezing point, but at no other temperature Let δn_0 molecules of solvent leave the solution and enter the solid state, which thus gains δn_0 molecules This all takes place at constant temperature and pressure, so that the total change in thermodynamic potential is zero. Now the thermodynamic potential of the solution has decreased by $(\varphi_0 - R\,ln\,x_0)\delta n_0$ owing to the departure of δn_0 gram moles, each of which had contributed $(\varphi_0 - R\,ln\,x_0)$ to the total Φ. On the other hand, that of the solid has increased by $\varphi_0'\delta n_0$ owing to the accretion of δn_0 molecules, where φ_0' is the thermodynamic potential of one gram molecule of solid. Naturally, no concentration term enters into this.

Thus $\quad (\varphi_0 - R\,ln\,x_0)\delta n_0 - \varphi_0'\delta n_0 = 0,$

therefore $\quad \varphi_0 - \varphi_0' = R\,ln\,x_0$

This equation applies at the freezing point of the solution. When we are dealing with the pure solvent $x_0 = 1$. Thus, at the freezing point of the pure solvent

$$\varphi_0 - \varphi_0' = 0$$

Let the freezing point of the solution be Δ lower than that of the pure solvent. Then Δ is the amount by which the temperature must be changed to bring $\varphi_0 - \varphi_0'$ from the value zero to the value $R\,ln\,x_0$.

Therefore $\quad -\Delta\frac{\partial}{\partial\theta}(\varphi_0 - \varphi_0') = R\,ln\,x_0,$

but we know that $\quad \left(\frac{\partial\varphi_0}{\partial\theta}\right)_p = \frac{u_0 + p_0 v_0}{\theta^2},$

as shown at the beginning of this section.

$$R\,ln\,x_0 = -\frac{\Delta}{\theta^2}[u_0 + p_0 v_0 - (u_0' + p_0' v_0')]$$

Since $p_0 = p_0'$ the expression in the bracket becomes

$$u_0 - u_0' + p(v_0 - v_0')$$

This clearly equals λ, the latent heat of fusion,

thus $\quad R\,ln\,x_0 = \frac{-\Delta\,\lambda}{\theta^2},$

but $\quad x_0 = \frac{n_0}{n_0 + n_1}$ and $x_1 = \frac{n_1}{n_0 + n_1},$

therefore $\quad x_0 = 1 - x_1,$

and $\quad R\,ln\,(1 - x_1) = -\frac{\Delta\;\lambda}{\theta^2}$

If, then, x_1 is small, as in the dilute solutions we are considering

$$-x_1 = ln\,(1 - x_1),$$

therefore $$x_1=\frac{\Delta\,\lambda}{R\theta^2},$$

or $$\Delta=\frac{R\theta^2}{\lambda}\,x_1,$$

the familiar result

The method here employed is the important thing to observe* The change in thermodynamic potential of the liquid solvent due to the presence of the solute—which does not affect the solid phase of the solvent—has to be neutralised by a change in temperature of the whole system This change can be calculated when the temperature coefficients of φ are known in terms of other thermal properties as we have seen

ACTIVITY

If one gram molecule of a substance is transferred from a solution where its concentration is C_1 to a solution where its concentration is C_2, the work done is $R\theta\, ln \frac{C_1}{C_2}$, if the substance behaves in accordance with van't Hoff's law In more concentrated solutions van't Hoff's law is not followed, and the expression $R\theta\, ln \frac{C_1}{C_2}$ ceases to be even approximately exact

For some purposes it is convenient to express the work done still in the form $R\theta\, ln \frac{a_1}{a_2}$, a_1 and a_2 being called the 'activities' of the substance in its two states

Having measured the work done in one of the various possible ways, for example by an electromotive force measurement, the ratio $\frac{a_1}{a_2}$ can be calculated a_1 and a_2 cannot be found separately. By convention, however, some standard state is selected in which the activity is taken arbitrarily as unity The activity in any other state may then, of course, be calculated from an appropriate measure of the work done

The sort of way in which activity is used may be illustrated by the aid of one example, the thallium amalgam concentration cell (G N. Lewis) This cell has two electrodes consisting of thallium amalgams of different concentrations dipping into a solution of a pure thallous salt. When a Faraday of electricity passes a gram molecule of thallium leaves the more concentrated amalgam and is deposited into the weaker amalgam

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* It is followed, for example, in the important paper of Debye and Hückel on the theory of solutions of strong electrolytes

If we regarded the thallium amalgams as very dilute with respect to thallium, we would find by applying van't Hoff's law to the dissolved thallium,

$$nEF=R\theta\, ln\, \frac{C_1}{C_2}$$

But to amalgams containing anything from 0 to 100 per cent thallium we can apply the equation

$$nEF=R\theta\, ln\, \frac{a_1}{a_2},$$

with its *ad hoc* defined 'activities' of the thallium in its different states

For very dilute amalgams the activity is taken as equal to the 'molecular fraction' of the thallium, i e practically to the concentration

The activity at any other concentration or molecular fraction is found as follows A series of electromotive force measurements are made with one amalgam (activity a_1, constant) as one electrode and different amalgams (activities denoted by a_2) as the other electrode These measurements are expressed by the equation

$$nEF=R\theta\, ln\, \frac{a_1}{a_2},$$

whence $$ln\, a_2 = ln\, a_1 - \frac{nEF}{R\theta}$$

Subtracting from each side $ln\, x_2$ where x_2 is the concentration of the thallium in the dilute amalgam, expressed as a molecular fraction,

$$ln\, \frac{a_2}{x_2} = ln\, a_1 - \left(\frac{nEF}{R\theta} + ln\, x_2\right)$$

It will be seen that when $x_2=0$, i e infinitely dilute amalgam, a_2 is by hypothesis equal to x_2 Thus

$$\frac{a_2}{x_2}=1 \text{ and } ln\, \frac{a_2}{x_2}=0$$

Therefore $$ln\, a_1 = \frac{nEF}{R\theta} + ln\, x_2$$

The procedure, therefore, is to plot $\frac{nEF}{R\theta} + ln\, x_2$ against x_2, and to read off its value for $x_2=0$ This value gives $\ln a_1$ Having found a_1, all the other activities can be calculated In this way a table can be compiled giving the 'activity' of the thallium in an amalgam of any strength

This is now often regarded as a very good conventional way of recording experimental results

CHAPTER VII

THE FOUNDATIONS OF THE PHASE RULE

It is assumed that the reader is familiar with elementary ideas of heterogeneous equilibrium, and the meaning of such terms as solubility curve and eutectic point The object of the present chapter is not to discuss detailed applications of the Phase Rule, but to deal with its thermodynamic basis, and to illustrate the lines along which the thermodynamic results are to be interpreted in terms of the kinetic theory of matter

The Phase Rule defines the conditions under which a system made up of various chemical species in their several physical states of aggregation can exist in a state of equilibrium

Three definitions must first be established—namely, those of component, phase, and degree of freedom

Component is best defined by saying that the number of components of a system is the minimum number of different substances starting from which the system can be brought into existence Thus, if the conditions are such that no chemical action takes place in the system, the number of components is simply the number of different substances which are present A slight complication arises only when there is chemical action so that some of the substances present at equilibrium need not have been added to the system as it was originally constituted, but may have been produced in it from others by chemical change An example, however, will make perfectly clear how the number of components is to be found in a case like this

Consider the system nitric oxide, nitrogen, oxygen First we must decide once and for all whether we propose to consider the system at a temperature so low that the velocity of union of nitrogen and oxygen, or of decomposition of nitric oxide, is so slow as to be negligible, or whether we propose to consider the system under such conditions that chemical equilibrium is established according to the equation $N_2+O_2\rightleftharpoons 2NO$ Thermodynamics has nothing to do with the rate at which a chemical change takes place, and will yield information about the system N_2, O_2, NO (no chemical change) as readily as about the system $N_2+O_2 \rightleftharpoons 2NO$ (chemical equilibrium established) The two systems are different systems from the thermodynamical standpoint, and it is no paradox that the number of components differs in the two cases In the first case the number of components is obviously three It is postulated that chemical change does not occur, hence nitrogen, oxygen, and nitric oxide must be added to the system as such Beyond the postulate that no chemical change occurs, there is no restriction to be imposed Any results obtained will be generally valid, subject only to the limitation of the postulate, although naturally they will only have a useful application when the conditions in practice are such that the assumption of no chemical change is permissible , that is to say, at low temperatures

In the second case, where we consider the system in which chemical equilibrium always prevails, the number of components is two instead of three This is because we can start, say, with nitrogen and oxygen, and allow the nitric oxide to be formed from them *in situ*. It might be thought that the number of components is one only, since both nitrogen and oxygen can be introduced into the system by the decomposition of nitric oxide But to see that this is false we have only to reflect that nitric oxide must always decompose into equal parts by volume of oxygen and nitrogen Thus, all possible mixtures of nitrogen, oxygen, and nitric oxide could not be prepared by the decomposition of nitric oxide We could obtain any ratio of nitric oxide to nitrogen, but the ratio of nitrogen to oxygen (by volume) in all the systems producible in this manner would be unity. To produce any desired proportions we should have to allow nitric oxide to decompose, and simultaneously introduce one or other of the two products so as to adjust the ratio of nitrogen to oxygen to the required value Hence the system must be regarded as a two component system If we wish for a special purpose to treat the case in which nitrogen and oxygen are only present in the proportions in which they are derived from nitric oxide, then for this special purpose we may treat the system as a one component system, but any results we derive will remain subject to this limitation.

The Phases of a system are the portions of it which are separated by boundary surfaces , or, as it is sometimes expressed, the 'physically distinct, mechanically separable' portions of a system Examples are too obvious and familiar to need mentioning

The number of degrees of freedom of a system is the number of variables determining the state of the system which must be arbitrarily fixed in order that the state of the system may be completely defined * This requires a little further elucidation First, with regard to the variables which determine the state of the system we may say that these comprise the following the concentration of each component in each phase, the temperature, the pressure, the geometrical nature of the boundary between each pair of phases, and the electrical condition of the system In exceptional cases other factors, such as magnetic state, may come in It is clear that if all these variables are known the system is completely described

But we find that they cannot all vary independently, and that when definite values are assigned to a certain number of them, then all the others are automatically determined The number of variables to which definite values can be assigned before the state of the system becomes uniquely determined is called the number of degrees of freedom of the system

For most purposes the only variable factors whose influence need be considered are temperature, pressure, and the various concentrations Most systems may be regarded as at a uniform electrical potential equal to that of the earth, so that the electrical conditions may be regarded as uniform and constant The equilibrium between two phases can be shown easily to depend upon the radius of curvature of the boundary surface (or, strictly speaking, the two principal radii of curvature) For example, the temperature at which a drop of water is in equilibrium with water vapour depends upon the radius of curvature of the drop, that is to say, upon the size of the drop, but it is also easily ascertainable that except in the case of very small drops the effect is small When two phases are present in considerable amount the radius of curvature of the boundary is large, or, in other words, the surface of separation is sensibly plane, and the influence of radius of curvature upon the equilibrium between the phases becomes quite negligibly small It is also obvious that the equilibrium between two phases with a plane surface of separation is independent of the absolute amounts of the

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* This use must not be confused with the meaning of the expression 'degree of freedom,' used in the mechanical sense in Chapter I

phases present, so that the geometrical nature of the boundary is without influence Our variable factors thus reduce to concentrations, temperature, and pressure

In all systems where these qualifications exist, that is to say, where electrical effects are absent, and there are no very small particles or surfaces of separation of small radius of curvature, generally speaking in all except colloidal systems, the phase rule now takes the form

$$P+F=C+2,$$

where P=number of phases, C=number of components, F=number of degrees of freedom

DERIVATION OF THE PHASE RULE

Suppose we have a system of C components in P phases, subject to the above limitations. The number of variable factors may easily be counted up First, the proportions of each component in each phase must be known But these are known if the proportions of $(C-1)$ components in each phase are given If, for example, the proportions are expressed in percentages by volume, and the percentages of $(C-1)$ components in a given phase amount to x per cent, then the percentage of the remaining component cannot be anything but $(100-x)$ Hence, for the P phases $P(C-1)$ proportions or concentrations must be given In addition, the temperature and pressure of the system must be known; for thermal and mechanical equilibrium of the system, of course, the temperature and pressure must be the same in each phase This completes the number of variable factors, because we suppose capillary and electrical effects to be absent Thus, we have

$$\text{Number of variables}=P(C-1)+2$$

These, as we have said, are not independent Ice, water, and water vapour of given vapour pressure cannot, for example, exist at any arbitrarily chosen temperature In fact, the three phases can only exist in equilibrium at one fixed temperature, and then under a definite vapour pressure Hence 'functional relationships' must exist between some of the variables The problem is now to investigate these relationships

To begin with, we have already said that thermal and mechanical equilibrium demands equality of temperature and pressure in all the phases This really involves a series of relations $\theta_1=\theta_2$, $\theta_2=\theta_3$, $p_1=p_2$, $p_2=p_3$ etc, which reduce what would have been $2P$ variables to 2 only The question of concentrations is, of course, not touched, and we now need relations determining the equilibrium of material between the various phases

The whole system is at constant temperature and pressure Hence, the thermodynamic criterion of equilibrium is that for any small virtual change subject to the constant temperature and pressure condition $d\varphi=0$, where φ is the thermodynamic potential of the system (p 120) Now φ is a function of all the concentrations in each phase For $\varphi=\Sigma\varphi_1$ where φ_1, φ_2, etc, are the thermodynamic potentials of the several phases, thus $\varphi=\Sigma\{U-\theta S+pv\}$ and U, S, and v clearly depend on the concentrations of the components It must be emphasised that φ depends upon the concentrations as well as on p and θ The importance of this fact will appear in a moment

Now we obtain the relations governing the material equilibrium by equating to zero all possible virtual changes in φ at constant temperature and pressure due to virtual changes in the various concentrations

There are P phases Each must be in equilibrium with all the others But since it is obvious that two phases which are respectively in equilibrium with a third phase are also in equilibrium with one another, we need only consider the equilibrium between the first and the second, the second and the third, and so on, that is to say, between $(P-1)$ pairs of phases

Take one pair, and, while everything else remains constant, let a small quantity da of one of the components pass from the first phase to the second Nothing else changes in the whole system This virtual change thus produces in φ the change $d\varphi=\frac{\partial\varphi}{\partial a}da$ But for equilibrium $d\varphi=0$, and since da is not zero $\frac{\partial\varphi}{\partial a}=0$

The importance of choosing for the discussion of the equilibrium conditions a quantity like φ, which is a function of the concentrations, is clear, since, if one had chosen, say, θ, $\frac{\partial\theta}{\partial a}$ is clearly zero, θ being independent of a, and the information that $0=0$ is not of much value, though in special cases it may be true

Similarly, considering the same pair of phases, we arrive at similar relations $\frac{\partial\varphi}{\partial b}=0$, etc, for each of the other components Thus, to express the equilibrium between this pair of phases we have C relationships of this form

But the equilibrium of the whole system is governed by the equilibrium between $(P-1)$ pairs of phases, thus we have

$$\text{Number of functional relationships}=C(P-1)$$

It is well known that n separate and independent equations completely define the values of n variables

The $C(P-1)$ equations which we have just seen to exist will fix the values of $C(P-1)$ variables But $P(C-1)+2$ variables are necessary to describe the state of the system Of these $P(C-1)+2$, therefore, $C(P-1)$ are fixed The difference, $P(C-1)+2-C(P-1)$, gives the number of variables which are not fixed, and may be given any values we like They are the degrees of freedom Thus

$$F=P(C-1)+2-C(P-1)=-P+2+C,$$
$$P+F=C+2.$$

SOME SPECIAL POINTS CONNECTED WITH THE APPLICATION OF THE PHASE RULE

The ordinary applications of the phase rule to simple cases of heterogeneous equilibrium are familiar and need not detain us here. Certain points, however, frequently present difficulty, and may be briefly discussed, although they are not part of the argument of this chapter

The first relates to the question of pressure and vapour pressure The difficulty may be illustrated in the following way. Consider a bell-jar standing over water, the air space in the jar being saturated with water vapour. We are tempted to apply the phase rule to the water and its vapour, putting $C=1$, and $P=2$, which gives us $F=1$ Hence, we might conclude that if the temperature be fixed the pressure will also be defined As regards the vapour, it is true enough that the vapour pressure has a definite value at a definite temperature, but as regards the liquid, it is quite untrue to say that at a given temperature we cannot vary the pressure on the liquid without causing a phase to disappear The error we have committed, however, is that we have regarded as a one component system what is really a system of more than one component. If we wish to regard liquid and vapour as a one component system, we must have the space above the liquid vacuous except for the vapour of the liquid itself There must be no air or other gas present Then, of course, no extra pressure can be transmitted to the liquid without simultaneously appearing in the vapour as increased vapour pressure which at once causes condensation The whole system is then truly monovariant The case of liquid having above it an inert gas saturated with the vapour of the liquid must be treated as follows Suppose the gas be nitrogen rather than air, so that only one foreign gas need be dealt with The system is now a two component system, and has two degrees of freedom If the temperature be fixed one degree of freedom is left There are, however, three variables, namely, pressure, concentration of nitrogen dissolved in liquid, concentration of vapour of liquid in gas phase. Pressure now has no ambiguous meaning It is equal to the sum of the actual vapour pressure of the liquid and the actual pressure of the nitrogen, and this sum is naturally equal to the hydrostatic pressure of the liquid If, now, this total pressure be fixed the whole system is defined, the concentration of the nitrogen in solution is fixed and the partial pressure of the vapour of the liquid in the gas space is fixed This is quite in accord with experience If excuse is needed for introducing a discussion of this rather obvious point, it must lie in the observed phenomenon that many students find it more of a stumbling block than the actual proof of the phase rule or its application to quite complicated systems

Another point worthy of mention at this point relates to the form which the phase rule assumes when applied to the so-called condensed systems Here the pressure on the system is greater than the vapour pressure of all the substances present The gas phase, therefore, disappears completely The phase rule then takes the form

$$P+F=C+1.$$

THE CASE WHEN CAPILLARY EFFECTS ARE NOT NEGLIGIBLE

When there are large surfaces of separation, as in all colloidal systems, the equilibrium between two phases is influenced by the condition of the boundary

Suppose we have two liquids only partially miscible If they form two bulky layers, then the influence of the surface of separation is negligible The phase rule is applied in the form $P+F=C+2$ We know from this that their mutual solubility is fixed at a given temperature and pressure Now, suppose one is shaken into fine drops dispersed in the other, so as to form an emulsion The solubility now depends upon the size of the emulsion droplets The radius of these is a new degree of freedom The phase rule now assumes the form

$$P+F=C+3$$

DISCUSSION OF THE PHASE RULE FROM THE STANDPOINT OF THE KINETIC THEORY

The foregoing thermodynamic arguments leave us in the dark as to the mechanism behind the phenomena of heterogeneous equilibrium It will now be useful to interpret some of the phase rule results in terms of the kinetic theory

Let us begin with a simple instance and compare the two systems

$$\underset{\text{(vapour)}}{NH_4Cl} \rightleftharpoons NH_3+HCl$$

$$\text{Solid benzene} \rightleftharpoons \text{liquid benzene}$$

We will regard the first system as a one component system, that is to say, preclude the addition of excess of either ammonia or hydrogen chloride The system is of one component in one phase, so that the number of degrees of freedom is two We may therefore fix the pressure arbitrarily and have a degree of freedom left over That is to say, the degree of dissociation will vary continuously with the temperature

In the case of the system, solid benzene, liquid benzene, we have one component as before, but two phases (In order that vapour shall be absent the pressure is to be assumed greater than the vapour pressure) Thus, there is only one degree of freedom, and if the pressure be fixed there is only one temperature at which solid and liquid benzene exist in equilibrium There is a sharp contrast between this system and the ammonium chloride system, for a change of temperature, instead of producing a corresponding change in the proportion of liquid to solid, causes the complete disappearance of one of these phases To see the kinetic interpretation of the fact that the presence of an extra phase destroys a degree of freedom, we will first see why it is that, under a given pressure, solid and liquid can only be in equilibrium at one temperature, whereas in a one phase system a complete equilibrium-temperature curve can be traced

Consider a plane face of the solid of unit area in equilibrium with the corresponding liquid Let the whole system be under any fixed pressure, large enough only to ensure the absence of vapour The equilibrium between the solid and liquid is a dynamic one, molecules of the solid continually passing into the liquid phase, while in a given time an equal number of molecules leave the liquid phase and take up positions on the face of the solid Regarding the solid as crystalline, we should say that growth and dissolution are taking place at equal rates, but independently of one another Let us regard the two processes separately for a moment The growth of a crystal face depends upon the retention of such molecules from the liquid phase as may approach it suitably orientated, and perhaps with appropriate velocities In the converse process certain molecules leave the face of the solid, having acquired by chance, in the course of the thermal agitation, an outwardly directed kinetic energy large enough to enable them to overcome the attractive forces retaining them in the solid structure It is easily seen that the two opposing processes are distinct in nature from one another The rates at which they occur are quite independent Both rates will clearly be influenced by pressure, which affects the closeness of packing of the molecules, and by temperature, but again independently of one another, and not to the same extent quantitatively For a given pressure there will be a certain rate of growth, dependent on temperature in one way, and a certain rate of dissolution, dependent on temperature in another way Each rate could be plotted against temperature in the form of a curve At a certain point the curves would cut, that is, at a certain temperature the two opposing rates are equal This is, of course, the temperature at which solid and liquid are in equilibrium under the given pressure and is therefore the melting point If the temperature is raised slightly, one of the rates becomes greater than the opposing rate As a matter of fact, it may be shown that a rate like the rate of dissolution which depends upon the acquirement by certain molecules of an excess of energy is much more increased by a rise in temperature than a rate like that of solidification which depends simply on the approach of the molecules to the surface Hence, when the temperature is increased it is the rate of melting which overtakes the rate of solidification , but we need not go into detail over this, since it is sufficient from the point of view of the phase rule to know that *one* of the rates becomes greater than the opposing one The phase rule does not say *which* phase disappears when the temperature of a non-variant system is changed Supposing the temperature to rise slightly above the melting point molecules begin to leave the surface of the solid more rapidly than they return Now, the all-important thing from the point of view of the present argument is that the *liquid is quite unaltered by a fresh influx of molecules of the same species as those of which it is already composed* Hence the rate at which it yields molecules to the solid is unaltered The increased rate of dissolution of the solid leads to no change in the liquid whereby the opposing rate of solidification can be increased There is no reaction whatever to the increased rate of melting relative to the rate of solidification Hence the change proceeds without check until the solid has completely melted In a precisely analogous way, in any one component two phase system at constant pressure, a displacement of the temperature from the equilibrium value causes the velocity of transition of one phase into the other to become greater or less than the reverse change The system being of one component and the pressure being constant, no concentration changes can come into play by way of counterbalancing this Hence the system must change until one or other of the phases has disappeared *entirely* Other examples similar to the case of melting just described can easily be thought out, and the generality of this statement will then be clearly seen

In the case of ammonium chloride, the existence of the system in one phase instead of in two phases makes a fundamental difference Consider the system in equilibrium under a fixed pressure at a given temperature The undissociated ammonium chloride vapour corresponds to the solid in the previous example, the equimolecular mixture of ammonia and hydrogen chloride, regarded as a single whole, corresponds to the liquid of the previous example Equilibrium is maintained by the equality of the two opposing processes, rate of dissociation and rate of recombination Just as before, these rates are independent and independently influenced by temperature and pressure Let the temperature be raised slightly, the pressure being kept constant One of the rates, say, the rate of dissociation, now predominates over the other.

Thus more ammonium chloride dissociates This does not go on indefinitely, however, as when the solid-liquid equilibrium was displaced, since a counteracting influence is immediately called into play The concentration of the dissociation products is increased relatively to that of the ammonium chloride, and the rate of recombination increases from this cause relatively to the rate of dissociation until both become equal again This compensating reaction cannot occur when the equilibrium is between two phases of a pure substance, because, as we have pointed out, the nature of a phase is unchanged by a mere addition of fresh material to it.

It is easy to see that the conclusion drawn from a comparison of these two systems is quite general We are thus justified on kinetic grounds in saying that, if for a system with a given number of components we increase the number of phases by one, we decrease the number of degrees of freedom by one This can be further extended Consider the system

$$\text{Solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Vapour}$$

The kinetic theory of the liquid, vapour equilibrium, was discussed in Chapter V, page 92, when it was seen that at a given temperature the vapour pressure must have a fixed value Thus, in the system we are considering, the pressure is fixed This being so, the simultaneous existence of the solid-liquid equilibrium demands that the temperature shall have a definite value Hence there are no degrees of freedom as compared with the one degree of freedom we had when only two phases were present

We may thus generalise a step further and say that, for a given number of components, the introduction of each fresh phase leads on kinetic grounds to the reduction of the number of degrees of freedom by one

Now let us consider the addition of another component We will take two examples first, the case of two solids which do not form mixed crystals and whose corresponding liquids form a single phase, and secondly, the case of two solids which form mixed crystals in all proportions

Solid and liquid in a one component system under a given pressure can only exist in equilibrium at one temperature This has already been shown Two component systems have, according to the phase rule, an extra degree of freedom Thus, a solid *A* can exist in equilibrium with liquid composed of *A* and *B* over an extended range of temperature Similarly with solid *B* Solids *A* and *B*, however, are only in equilibrium simultaneously with the liquid at one temperature, the eutectic temperature We have now to see that this result follows simply from the kinetic theory

Consider a plane face of solid *A* in equilibrium at a given temperature with liquid composed of *A* and *B* The rate of deposition of molecules of *A* from the liquid on to the face of the solid is equal to the rate at which molecules leave the face of the solid and enter the liquid Molecules of *B* are not deposited on *A*, the two substances being assumed not to be miscible in the solid state Let the temperature be changed slightly, so that the rate of melting of *A* is increased. Were the liquid pure *A*, then all the solid would melt But in the present case, when a certain amount of the solid *A* has dissolved, the concentration of *A* in the liquid will have increased, and for this reason the rate of return of molecules to the solid will increase until it is once more equal to the rate of leaving Hence at a new temperature a new equilibrium is established between solid *A* and a liquid of different composition from the original liquid The presence of the second component *B* in the liquid introduces a concentration effect on the velocity of return, which enables the system to react to a change in the rate of melting of *A* This was absent in the case of the pure liquid

Similarly, equilibrium between solid *B* and the liquid will be possible over a whole range of temperatures, since a change in the rate of melting of *B*, brought about by a change in temperature, can be counterbalanced by a change in the rate of return of molecules to the solid as the concentration of *B* in the mixed liquid varies Here, then, we see that an extra component introduces an additional degree of freedom

At a given pressure we cannot have both solid *A* and solid *B* in equilibrium with the liquid over a continuous range of temperature For let us consider a particular temperature in the range where *A* can exist in equilibrium with liquid The rate at which molecules leave the surface of solid *A* is fixed at a given temperature Thus the concentration of *A* in the liquid will adjust itself to such a value that the rate of deposition equals this The concentration of *A* in the liquid being thus fixed, that of *B* is also fixed But this automatically determined concentration of *B* will not in general be equal to that which would produce a rate of deposition of *B* equal to the rate of melting of solid *B* We might suppose it to be greater than this, only that in this case more *B* would solidify, thus leaving more *A* in solution, so that more *A* would solidify, and we should end with solid *A* and solid *B* and no liquid This would, of course, correspond to a temperature below the eutectic point, it does not correspond to the case postulated, namely, that solid *A* shall be in equilibrium with liquid We must therefore conclude that the concentration of *B* in the liquid is smaller than that required for equilibrium with solid *B*, so that all the solid *B* dissolves Similarly, when solid *B* is in equilibrium with liquid, it will be seen that in general all *A* must dissolve We thus see from the kinetic standpoint that we can plot curves giving the concentration of liquid which is in equilibrium with solid *A* and solid *B* respectively at various temperatures At one temperature, where these curves cut, the composition of the liquid which is in equilibrium with *A* will coincide with that which is in equilibrium with *B* Here, and only here, the two solid phases may exist in equilibrium with liquid Incidentally, we see again that the addition of a phase removes a degree of freedom

A and *B* may be present together in the solid state without introducing two phases if they form a solid solution The phase rule tells us that a solid solution of *A* and *B* can exist in equilibrium with liquid not merely at a single temperature, but over a range of temperatures The kinetic interpretation of this is clear

First consider *A* and *B* as separate solid phases in equilibrium with the liquid at the eutectic temperature Let the temperature be raised slightly As we have just seen, the composition of the liquid cannot adjust itself to remain in equilibrium with both solid *A* and solid *B*, so that for one of them the rate of melting exceeds the rate of solidification, and all of this one dissolves Now compare the case of a solid solution of *A* and *B* in equilibrium with the liquid at same temperature The rate at which molecules of *A* leave the surface of the solid solution is equal to the rate at which they return, and similarly for *B* But the number of molecules of *A* which leave unit area of the solid in unit time is no longer an invariable quantity The surface now consists of molecules of *A* intimately mingled with molecules of *B*, so that the number of molecules of *A* which leave in a given time depends upon the concentration of *A* in the solid solution When the temperature is raised we shall find, as before, that the liquid which provides a suitable rate of return of molecules of one kind to the solid phase will provide too small a rate for molecules of the other Suppose it is B whose molecules are now leaving the solid more rapidly than they are returning Were we dealing with pure B in the solid phase it would all melt, but, since we now have a concentration effect in the solid phase as well as in the liquid phase, molecules of B will merely pass into the liquid until the concentration of B in the solid solution, and hence the rate at which molecules leave the solid, falls once more to an equilibrium value Hence we see once more, then, an extra degree of freedom appears when we diminish the number of phases by one

It should be clear from the foregoing discussions that (a) for a given number of phases the introduction of each new component produces an additional degree of freedom, while (b) for a given number of components the introduction of each new phase causes a degree of freedom to disappear Thus, when C is constant $P+F$ is constant, while when P is constant $F-C$ is constant On combining the two results $P+F-C=$constant To evaluate the constant, we consider the special system of 1 component in 3 phases, which we saw on kinetic grounds to be non-variant Here $P=3$, $C=1$, $F=0$ Whence, constant$=3+0-1=2$

Thus $P+F-C=2$, or $P+F=C+2$, and we see that quite general kinetic considerations lead to the same result as the thermodynamic investigation To render the mechanism clear we have proceeded by a process of induction, but the derivation could have been made quite general

It is a mistake to think that most thermodynamic results cannot be visualised in terms of molecular theory That is why we have devoted some space to a discussion of this problem

CHAPTER VIII

THE PROBLEM OF CHEMICAL COMBINATION

THE problem of what is often called chemical affinity has aroused interest from the earliest days of chemistry. But before we can proceed to investigate what results are yielded by the application of thermodynamics to the question, we must first decide clearly what we mean by the term ‘affinity,’ which is frequently used in an ambiguous way.

The first point to recognise clearly is that all chemical reactions are, if only to an immeasurably small extent, reversible. A chemical equilibrium, dynamic in nature, is established by the balancing of the rates of two opposed reactions. It frequently happens that in such a change as

$$\underset{\text{1 molecule}}{A} + \underset{\text{1 molecule}}{B} \rightleftharpoons AB$$

the amounts of A and B which remain uncombined at equilibrium are extremely minute, and the reaction can be regarded for practical purposes as irreversible. In an example like this it is just to say that the affinity of A for B is great. At a different temperature the amounts of A and B remaining uncombined at equilibrium might be much larger. The affinity of A for B would be less than before. At yet another temperature the compound AB might be very largely dissociated at equilibrium. This would mean that the affinity of A for B was small. It is the *extent* to which a reaction has proceeded when the equilibrium point is reached which measures the affinity of the combining substances for one another. The equilibrium constant is the quantity on which we must fix our attention in seeking a quantitative measure of affinity.

It is necessary to draw a very clear distinction between affinity and ‘reactivity.’ Because oxygen and hydrogen at ordinary temperatures may exist together without combining it must not be said that the affinity is small. Their reactivity is low; that is to say, the rate of combination is small, but when equilibrium is finally established—even though a very great time is required for its establishment—

then they are found to have combined almost completely The equilibrium constant

$$\frac{[H_2O]^2}{[H_2]^2[O_2]}$$

is large, and this is what we mean when we say that the affinity is great

There is no sort of correlation between affinity and reactivity, it might be thought that in general substances with a large affinity for one another would combine more rapidly than those with little affinity, but the cursory consideration of a few cases like that of oxygen and hydrogen at ordinary temperatures soon shows that no such relation exists The reverse is indeed very often true It has been shown that in the reaction $4H \rightleftharpoons He$, which according to our views of atomic structure is theoretically possible, the formation of helium at equilibrium should be almost complete and that the affinity should be much greater than in any of the more ordinary chemical reactions Yet the velocity is so small that no trace of such helium synthesis has ever been detected This extreme instance may help to emphasise the complete lack of correlation between reactivity and affinity Usually, however, the equilibrium point can be reached by suitable means Therefore the discussion of equilibrium relations without reference to reactivity is quite as important as that of reaction velocity From the practical point of view both aspects of the subject naturally have to be considered

With regard to reactivity thermodynamics yields practically no information, while with regard to the problem of affinity it yields an almost complete solution We must first decide upon a *quantitative* measure of affinity In the case of a gaseous reaction, a reaction in dilute solution, or indeed any homogeneous reaction it might be thought that the value of the equilibrium constant K, and its variation with temperature according to the equation,

$$\frac{d \ln K}{d\theta} = -\frac{U}{R\theta^2},$$

would define the situation quite adequately But for the purpose of further development, and incidentally to make possible a uniform treatment of both homogeneous and heterogeneous reactions, it is convenient to frame the formal definition of affinity in the following way When a reaction proceeds from a given initial state to a given final state the affinity is measured by the maximum work which the process can be made to yield. In other words the affinity is to be measured by the quantity A which was discussed at some length in Chapter IV. The advantages of this method of formulation are many. Let us take the example dealt with in Chapter IV, the water gas reaction. We found that starting with carbon monoxide and steam at concentrations C_1 and C_2 and converting them with the aid of an equilibrium box into carbon dioxide and hydrogen at concentrations C_3 and C_4 the maximum work is given by

$$A=R\theta\left\{ln\frac{C_1C_2}{C_3C_4}-ln\,K\right\}$$

A depends not only upon the nature of the substances taking part in the reaction, but also upon other conditions. Pure carbon monoxide and pure steam at certain temperatures have a great tendency to combine; that is to say, equilibrium is not established until a considerable proportion of carbon dioxide and hydrogen is produced. But when the concentrations of carbon dioxide and hydrogen have reached equilibrium values the tendency of carbon monoxide and steam to react further disappears. The affinity thus depends upon the conditions of concentration, and, as we have seen, when C_1, C_2, C_3, and C_4 are equilibrium values

$$ln\frac{C_1C_2}{C_3C_4}=ln\,K,\ \text{and}\ A=0$$

When C_1 and C_2 are greater than the corresponding equilibrium values and C_3 and C_4 less, then A is positive and the affinity in the direction of carbon dioxide and hydrogen formation is positive. When C_1 and C_2 are less than the corresponding equilibrium values, and C_3 and C_4 greater, then A is negative; that is to say, there is a negative affinity in respect of the direct reaction so that instead of carbon monoxide and steam reacting to yield carbon dioxide and hydrogen the reverse change takes place.

Berthelot's suggestion that the heat of reaction could be regarded as a measure of affinity is at once disproved by the fact that in any reversible reaction the affinity may be positive or negative according to the concentrations, while the heat of reaction is a constant quantity. Hydrogen and oxygen have a great tendency to combine at 2,000°, in the sense that they will combine to a very large extent, the value of $K=\frac{[H_2]^2[O_2]}{[H_2O]^2}$ being very small. It is true that the evolution of heat in the reaction is very large, so that this example is in accordance with the Berthelot principle. But pure steam at 2,000° tends to dissociate to a slight extent, that is to say that the endothermic dissociation has a positive affinity in contradiction to the Berthelot principle. We cannot therefore in any sense regard the heat evolution as a measure of the tendency of a reaction to take place, in the same way that the quantity A is a measure of this tendency.

Nevertheless it is very frequently found that in highly exothermic reactions the equilibrium constant, written with reactant terms in the numerator, is very small. Hence the reaction would have to proceed very far before the reversal of affinity occurred. In this sense Berthelot's principle is often an approximation to the truth, and we shall see later that the heat of reaction actually is one of several factors which determine the affinity. The Berthelot principle is part of the truth but not the whole truth.

With regard to heterogeneous reactions we have already seen that the quantity A is an effective measure of the tendency of such reactions as the conversion of grey tin into white tin to take place.

Having decided on the maximum work as the measure of affinity we must proceed to inquire what information the laws of thermodynamics yield about its magnitude in any given instance. We have already the following relationships—first the general relation applying to any isothermal change

$$A-U=\theta\frac{dA}{d\theta} \qquad (1)$$

We can apply this directly to any chemical change in which the volume change is negligible, and to others with simple corrections.

Secondly, applying to the special case of gas reactions, or reactions in dilute solution where osmotic laws analogous to the gas laws are obeyed,

$$A=R\theta\{\Sigma \ln C-\ln K\} \quad . \qquad (2)$$

and thirdly, applying to the same cases, the van't Hoff isochore

$$\frac{d\ln K}{d\theta}=\frac{U}{R\theta^2} \qquad (3)$$

THE PRINCIPLE OF LE CHATELIER

Before proceeding to develop these equations further a direct consequence of (3) must be discussed Endothermic compounds are formed to an increasing extent with rise of temperature, while exothermic compounds are more and more dissociated More generally the principle may be stated thus *Increase of temperature favours the production of the system which is formed with absorption of heat* This follows immediately from equation (3) U is the *decrease* in internal energy accompanying the progress of the reaction in the direction reactants → products, it is thus heat *evolved* A positive value of U thus represents an exothermic reaction When U is positive $\frac{d \ln K}{d\theta}$ must also be positive, or $\ln K$, and hence K itself, must increase with temperature But K is written with reactants in the numerator Hence as K increases reactants increase at the expense of the products Thus the products resulting from the exothermic reaction are less and less completely formed as the temperature increases The converse follows in the same way

The second law of thermodynamics gives us the exact equation

$$\frac{d \ln K}{d\theta} = \frac{U}{R\theta^2}$$

The particular inference from the equation which we have just drawn is, however, already implicit in the assumption that a stable equilibrium between reacting substances and products can exist at all This may be most simply seen by supposing that increase of temperature might favour the production of the system formed with evolution of heat Let products and reactants be in equilibrium at a given temperature in an adiabatic enclosure Let there be an infinitesimal displacement of equilibrium in the direction of formation of the products Heat is evolved, the temperature rises by an infinitesimal amount causing a further displacement of equilibrium in the *same direction* as before This involves further evolution of heat, and further accentuation of the original virtual displacement until finally the reaction proceeds to completion in this direction No stable equilibrium is thus possible unless increase of temperature leads to a displacement of equilibrium in the opposite sense to that just postulated namely, the displacement must be in the direction of the system formed with absorption of heat

INTEGRATION OF THE EQUATIONS CALCULATION OF TRANSITION POINTS AND EQUILIBRIUM CONSTANTS

Considering equations (1) and (3) let us see what information we may obtain if the equations can be completely integrated

$$A-U=\theta\frac{dA}{d\theta},$$

$$\frac{1}{\theta}\frac{dA}{d\theta}-\frac{A}{\theta^2}=-\frac{U}{\theta^2},$$

$$\text{that is } \frac{d}{d\theta}\left(\frac{A}{\theta}\right)=-\frac{U}{\theta^2},$$

$$\therefore \quad A=\theta\int-\frac{U}{\theta^2}+\theta J \tag{4}$$

To calculate A at any temperature we must know both U and the integration constant J If these are known A is given in terms of θ Knowing U and J, for the reaction grey tin → white tin for example, we could calculate the value of A at any temperature or conversely calculate the temperature at which $A=0$, that is the transition point

Similarly by integrating equation (3) we obtain

$$\ln K=\int\frac{U}{R\theta^2}+I \tag{5}$$

If U and I are known the absolute value of K at any temperature can be calculated

In equations (4) and (5) it must be borne in mind that U is not constant but varies with temperature On page 28 it was shown that

$$\frac{dU}{d\theta}=\begin{array}{c}\text{Sum of specific heats}\\ \text{of reactants}\end{array}-\begin{array}{c}\text{Sum of specific heats}\\ \text{of products,}\end{array}$$

$$=\Sigma\sigma_1-\Sigma\sigma_2$$

The specific heats themselves vary with temperature, so that we have

$$U=U_0+\int_0^\theta\Sigma\sigma_1 d\theta-\int_0^\theta\Sigma\sigma_2 d\theta,$$

and this value of U should be substituted in equations (4) and (5) when the integration is performed

The laws governing the variation of specific heats with temperature are complex, but the actual values of

$$\int_0^\theta \Sigma\sigma_1 d\theta - \int_0^\theta \Sigma\sigma_2 d\theta$$

can be expressed to any required degree of accuracy by a series $a\theta+b\theta^2+c\theta^3+d\theta^4$ $a, b, c\ d$ having values determined from the experimentally observed specific heats

Thus $\quad U=U_0+a\theta+b\theta^2+c\theta^3$

and equation (4) becomes

$$A=-\theta\int\frac{U_0+a\theta+b\theta^2+c\theta^3}{\theta^2}+\theta J,$$

or

$$A=U_0-a\theta\ ln\ \theta-b\theta^2-\frac{c\theta^3}{2}+\theta J \qquad (6)$$

and equation (5) becomes

$$ln\ K=\int\frac{U_0+a\theta+b\theta^2+c\theta^3}{R\theta^2}+I,$$

or

$$ln\ K=-\frac{U_0}{R\theta}+\frac{a\ ln\ \theta}{R}+\frac{b\theta}{R}+\frac{c\theta^2}{2R}+I \qquad (7)$$

U_0, a, b, c are purely thermal data, which must be determined experimentally—or, in principle at least, calculated from molecular forces *

The first and second laws of thermodynamics yield no information about the integration constants J and I Thus to calculate K at any required temperature we not only need to know the values of the various thermal quantities involved, but we must know the value of K at one particular temperature in order to substitute and find the value of I once and for all It might therefore be thought that A and K remain quite specific and undetermined by the thermal data But Nernst has shown that by the addition of another quite general principle to the laws of thermodynamics the problem may be solved

* Born and Lande have made some progress in this direction

NERNST'S HEAT THEOREM

Nernst first deals with the calculation of A for systems in which only liquid or solid substances are present, that is for condensed systems For these condensed systems—and it must be emphasised that the assumption to be made *only applies to condensed systems*—he assumes that *when* $\theta=0$

$$\frac{dA}{d\theta}=0 \text{ and } \frac{dU}{d\theta}=0$$

This assumption makes $J=0$, *so that* A *can be expressed in terms of* θ *without an undetermined integration constant*

For $$U=U_0+a\theta+b\theta^2+c\theta^3$$

$$\frac{dU}{d\theta}=a+2b\theta+3c\theta^2$$

when $\theta=0$ $\quad \frac{dU}{d\theta}=a=0$,

therefore $a=0$

Also from (6) $$A=U_0-a\theta \ln \theta-b\theta^2-\frac{c\theta^3}{2}+\theta J,$$

$$=U_0-b\theta^2-\frac{c\theta^3}{2}+\theta J,$$

$$\frac{dA}{d\theta}=-2b\theta-\frac{3c\theta^2}{2}+J,$$

when $\theta=0$ $\quad \frac{dA}{d\theta}=J=0$,

therefore $J=0$

Thus $$U=U_0+b\theta^2+c\theta^3, \qquad (8)$$

$$A=U_0-b\theta^2-\frac{c\theta^3}{2} \qquad (9)$$

Therefore when U is known as a function of temperature, A is also known

The justification of Nernst's theorem depends upon the fact that the calculations of A made from thermal data in this way agree with experiment Further there is direct evidence that $\frac{dU}{d\theta}$ becomes smaller as temperature falls

For example the difference between the specific heats of solid and super-cooled liquid becomes smaller as the temperature is lowered

CALCULATION OF TRANSITION POINTS

We have had many examples of the principle that at a transition point the quantity A becomes zero By the aid of Nernst's two assumptions we have now obtained an expression for A in terms of the thermal data U_0, b, c , and the temperature If this equation is solved for the value of θ corresponding to $A=0$ we obtain the transition point In particular from a knowledge of the latent heat of fusion and the specific heats of liquid and solid over a range of temperature it is possible to calculate the melting point of a substance

As an example of such a calculation we may take the following

Suppose the specific heat of one allotropic form of a substance in the immediate neighbourhood of 35° C is 0 314, and that of another allotrope in the immediate neighbourhood of the same temperature is 0 436 At 55° C let the corresponding values of the two specific heats be 0 343 and 0 473

Then we have

$$\frac{dU}{d\theta}=\text{difference between specific heats}$$

At 35° C, where $\theta=273+35=308°$,

$$\frac{dU}{d\theta}=0\ 436-0\ 314,$$

$$=0\ 122,$$

and at 55° C, where $\theta=273+55=328°$,

$$\frac{dU}{d\theta}=0\ 473-0\ 343,$$

$$=0\ 130$$

Now we have the equations (8) and (9)

$$U=U_0+b\theta^2+c\theta^3,$$

$$A=U_0-b\theta^2-\frac{c\theta^3}{2}$$

Differentiating the first we obtain

$$\frac{dU}{d\theta}=2b\theta+3c\theta^2$$

Substituting the numerical values

$$0\ 122=2\times 308b+3(308)^2\,c,$$
$$0\ 130=2\times 328b+3(328)^2\,c$$

The variation of $\frac{dU}{d\theta}$ with θ is here so small that the term $3c\theta^2$ is unnecessary and the expression $\frac{dU}{d\theta}=2b\theta$ is sufficiently accurate , whence we find $b=0\ 000198$ In principle however we can equally well solve for c also

Thus $$U=U_0+0\ 000198\,\theta^2,$$
$$A=U_0-0\ 000198\,\theta^2$$

If the latent heat of transformation at 58° be 40 0 calories per gram we have

$$40\ 0=U_0+0\ 000198\times(273+58)^2,$$

whence $$U_0=18\ 3,$$
$$A=18\ 3-0\ 000198\,\theta^2$$

If θ_m be the transition point, then

$$0=18\ 3-0\ 000198\,\theta^2_m$$

whence $$\theta_m=\sqrt{\frac{18\ 3}{0\ 000198}}=304^\circ$$

This gives the transition point as 31° C

Nernst first made such a calculation for the transition point of rhombic sulphur to monoclinic sulphur and obtained a value in satisfactory agreement with the observed value

The equation can be applied equally well to the calculation of the melting point of a substance, the melting point being merely the transition point from solid to liquid The only data required are the specific heats of the liquid and of the solid and the latent heat of fusion, but at the present time thermal data of sufficient accuracy are not available in a very large number of cases

THE EXPERIMENTAL JUSTIFICATION OF NERNST'S ASSUMPTIONS, AND THEIR THEORETICAL SIGNIFICANCE

It has already been said that the two assumptions

$$\left.\begin{aligned}\frac{dA}{d\theta}&=0\\ \frac{dU}{d\theta}&=0\end{aligned}\right\}\text{when } \theta=0$$

are made with the express purpose of causing the thermodynamically indeterminate integration constant of the Gibbs-Helmholtz equation to vanish in the case of solid and liquid systems The justification of the assumptions depends mainly upon the agreement with experience of consequences derived from them

The tests take three forms

1 Calculation of transition points from the condition $A=0$ This yields satisfactory results in all cases where the thermal data are known with sufficient precision to allow the calculation to be carried out

2 Comparison of the values of A derived from the equations given above with directly determined values of A The quantity A may be determined directly by (*a*) measurements of vapour pressure, (*b*) measurements of solubility, (*c*) measurements of electromotive force

Thus if the vapour pressures of solid and super-cooled liquid are measured we have $A=R\theta \ln \frac{p_{\text{liquid}}}{p_{\text{solid}}}$

If the solubilities of rhombic sulphur and of monoclinic sulphur in the same solvent are measured we have

$$A=R\theta \ln \frac{S_{\text{monoclinic}}}{S_{\text{rhombic}}}$$

Similarly the electromotive force of the cell grey tin, electrolyte, white tin is a measure, as we have already seen, of the affinity of the process, and can be calculated by means of Nernst's equations from the specific heats of the two forms of tin and the heat of transformation

Calculations of this sort justify the Nernst theorem One of the best experimental investigations of the matter is that of Bronsted (Z physikal Chem , 1914, 88, 479), which merits very careful study in the original

3 Direct evidence is available to show that $\frac{dU}{d\theta}$ diminishes steadily with fall of temperature

For $\frac{dU}{d\theta}=$ difference between specific heats of reactants and products

This has been found to diminish with θ in the case of rhombic and monoclinic sulphur, and in the case of several solids and super-cooled liquids Thus at 320° abs , the difference between the specific heats of liquid and solid betol is 0 067, at 240° 0 0355, and at 130° 0 004

Turning to the theoretical significance of the two assumptions we see that if $\frac{dU}{d\theta}=0$ at the absolute zero, then the specific heat of any compound at this temperature must be the sum of the specific heats of its component elements For consider the reaction

$$Fe+S=FeS$$

$\frac{dU}{d\theta}=$Specific heat of iron+Specific heat of sulphur—Specific heat of ferrous sulphide

If $\frac{dU}{d\theta}=0$ when $\theta=0$ it means that the molecular heat of ferrous sulphide is the sum of the atomic heats of iron and sulphur at the absolute zero In other words, at this temperature specific heat is an additive property

EXTENSION OF THE NERNST THEOREM TO THE CALCULATION OF GASEOUS EQUILIBRIA

By means of the van't Hoff equilibrium box a value of A may be derived for a gaseous transformation at constant volume This value may be substituted in the Gibbs-Helmholtz equation, and the integration performed But in this case we could not put the integration constant equal to zero, because the Nernst assumptions, which make the integration constant vanish, only apply to condensed systems A simple case illustrates their inapplicability where gases are concerned

For the expansion of a perfect gas from volume v_1 to volume v_2 the value of A is $R\theta\ ln\frac{v_2}{v_1}$ and

$$\frac{dA}{d\theta}=R\ ln\frac{v_2}{v_1}.$$

This is independent of θ, hence the relation $\frac{dA}{d\theta}=0$ when $\theta=0$ cannot hold

But by an indirect method Nernst's heat theorem may be applied to the calculation of gaseous equilibria, or, in other words, to the evaluation of the integration constant I of the equation

$$ln\ K=\int\frac{U}{R\theta^2}+I.$$

Suppose a chemical reaction such as the following, $CO+H_2O=CO_2+H_2$, to take place between the substances *in the solid state* The conversion of one gram molecule of solid carbon monoxide and one gram molecule of ice into carbon dioxide and hydrogen, also in the solid state, would, if conducted reversibly, yield a quantity of work A_s Since the whole transformation is taking place in the condensed state Nernst's theorem may be applied and A_s may be expressed in the form $A_s=U_s-b\theta^2$ without an integration constant

The value A_g for the affinity of the corresponding gaseous change is given by

$$A_g=R\theta\{\Sigma n\ ln\ C-ln\ K\},$$

where $$ln\ K=\int\frac{U}{R\theta^2}+I$$

If the relation between A_s and A_g can be found the constant I can be evaluated

It will be convenient for what follows to express K not in terms of concentrations but in terms of partial pressures and to write

$$A_g=R\theta\{\Sigma n\ ln\ p-ln\ K_p\},$$

where p represents the partial pressure of any gaseous component

K_p means the equilibrium constant with concentrations expressed in terms of partial pressure

The relation between A_s and A_g is found in the following way We first allow the reaction to take place in the solid state, thereby obtaining the work A_s We then achieve the same final result by first evaporating the reactants, allowing them to react in the gaseous state, and then condensing the products The total work yielded in this process must be equal also to A_s since the passage from the same initial state to the same final state at constant temperature must yield the same amount of work by whatever reversible path it is brought about

We proceed therefore to calculate the work done when the reaction is conducted in this indirect way

(i) 1 gram molecule of solid carbon monoxide is evaporated under its vapour pressure π_{CO} The work done is $R\theta$ 1 gram molecule of ice is also evaporated under the vapour pressure π_{H_2O} The work done is $R\theta$, making $2R\theta$ in all

(ii) The gases so obtained can be made to react by way of an equilibrium box The all-important point is that we choose the arbitrary final pressures of carbon dioxide and hydrogen so that they are equal to π_{CO_2} and π_{H_2} respectively, these being the saturated vapour pressures of the solid carbon dioxide and solid hydrogen.

The work done is

$$R\theta\left\{ln\frac{\pi_{CO}\ \pi_{H_2O}}{\pi_{H_2}\ \pi_{CO_2}} - ln\ K_p\right\}$$

(iii) The gram molecules of carbon dioxide and hydrogen can now be reversibly condensed to solid by the expenditure of work $2R\theta$, which cancels the corresponding term in (i) The operation is now complete The total work is given simply by

$$R\theta\{\Sigma n\ ln\ \pi - ln\ K_p\},$$

and this must be the same as A_s

Now since by Nernst's theorem A_s can be expressed in the form

$$A_s = U_s - b\theta^2$$

we have

$$R\theta\{\Sigma n\ ln\ \pi - ln\ K_p\} = U_s - b\theta^2$$

This is the fundamental equation for the rest of the discussion

EVALUATION OF THE INTEGRATION CONSTANT OF THE EQUATION

$$\frac{d\ ln\ K}{d\theta} = \frac{U}{R\theta^2}$$

From this differential equation we find

$$ln\ K_p = \int\frac{U}{R\theta^2} + I$$

It is required to find I

The last equation of the previous section involves terms such as $ln\ \pi$

For the variation of vapour pressure with temperature we have

$$\frac{d\ ln\ \pi}{d\theta} = \frac{\lambda}{R\theta^2},$$

whence

$$ln\ \pi = \int\frac{\lambda}{R\theta^2} + i$$

Substituting in the fundamental equation for $\ln \pi$ and $\ln K_p$ we find

$$R\theta\left\{\Sigma n\int\frac{\lambda}{R\theta^2}+\Sigma n i\right\}-R\theta\int\frac{U}{R\theta^2}-R\theta I=U_s-b\theta^2$$

The two sides of this equation are functions of θ We can therefore equate the coefficients of like powers of θ on the two sides In particular we shall equate the coefficients of the *first* powers of θ

The terms $R\theta\int\frac{\lambda}{R\theta^2}$ and $R\theta\int\frac{U}{R\theta^2}$ do not contribute any first powers of θ

Both expressions are of the same form, so that it will be sufficient to show this for one of them

$$R\theta\int\frac{U}{R\theta^2}=R\theta\int\frac{U_0+\alpha\theta+\beta\theta^2+}{R\theta^2},$$

$$=R\theta\left\{-\frac{U_0}{R\theta}+\frac{\alpha}{R}\ln\theta+\frac{\beta\theta}{R}\qquad\right\}$$

From this it is obvious that there is no term in the first power of θ contributed to the left hand side of the equation by these expressions The only such terms are $\Sigma n i R\theta$ and $-R\theta I$. Thus the coefficient of θ on the left hand side is

$$R\{\Sigma n i-I\}$$

On the right hand side there is no term in the first power of θ It will be remembered that the $a\theta$ term in $U_s-b\theta^2$ vanished as the *direct result* of the Nernst theorem

Thus we have

$$R\{\Sigma n i-I\}=0,$$

or

$$I=\Sigma n i$$

Thus the integration constant of the van't Hoff equation is seen to be the algebraic sum of the integration constants of the vapour pressure equations of the various corresponding solids (Reactants are counted as positive in forming this sum, products negative)

This means that, in principle at least, gaseous equilibria can be calculated *a priori* from purely thermal data Although accurate enough thermal and vapour pressure data are seldom available for very exact calculations, most valuable results are yielded by even approximate calculations of the order of magnitude of equilibrium constants The position of equilibrium in a reaction which has never been studied experimentally at all can be approximately foretold Reference should be made to many illuminating examples in Sackur's Berechnung Chemischer Affinitaten

EXTENSION AND QUALIFICATION OF THE BERTHELOT PRINCIPLE

The equilibrium constant of a gaseous reaction now assumes the form

$$ln\ K=\int\frac{U}{R\theta^2}+\Sigma ni$$

If we take U as constant, and doing this does not affect our argument qualitatively in the least, the equation becomes

$$ln\ K=-\frac{U}{R\theta}+\Sigma ni$$

Let us consider the two terms on the right side of the equation separately U is heat evolved K is expressed with the products of the reaction in the denominator thus a large value of K means very incompletely formed products, and a small value of K means stable products

When much heat is evolved, U is large and positive $-U$, therefore, has a large negative value $ln\ K$, likewise, has a large negative value This means that K is very small That is, the products are very completely formed This is exactly in accord with Berthelot's principle

A large value of Σni operates the other way, making K large, which means large dissociation of the products or very incomplete reaction

According to their signs $-\frac{U}{R\theta}$ and Σni may reinforce each other or counteract each other

As a matter of fact most values of i are of roughly the same order of magnitude, and Σn itself plays the most important part in fixing the sign of this term

If many molecules unite to form few in the reaction, Σn is large and positive Thus Σni is probably also large and positive This tends in the direction of increasing K, and thus operating against the formation of the products Let us take one simple example If a very large number of molecules of carbon, hydrogen, and oxygen be thought of as yielding cane sugar by synthesis Σni will be enormous $-\frac{U}{R\theta}$

will not be very large Hence K will be enormous That is to say, the amount of sugar synthesised at equilibrium is extremely minute—numerical calculation shows quite immeasurably small This influence of the $\Sigma h\nu$ term, therefore, may quite overcome the influence of the other There would then be no approximation to Berthelot's principle

The influence of a large value of Σh has a clear interpretation in terms of the theory of probability The extremely complicated sets of molecular encounters which would have to occur if a very complex body were to be formed by direct synthesis from its elements are so improbable that the yield of product at equilibrium is negligible

CHAPTER IX

ENTROPY AND PROBABILITY

FROM the beginning we have seen that the second law of thermodynamics is a direct and inevitable consequence of the very nature of matter and of heat All matter is built up of molecules, and the heat which it contains is the sum of the mechanical energies of all the individual molecules This energy may be of several forms First, it may be kinetic energy of translation, rotation, or vibration about a mean position, and internal energy due to the relative motion of the atoms constituting the molecule Secondly, it may comprise potential energy due to the separation of the molecules from one another despite attractive forces tending to draw them nearer together, or due to the displacement of unsymmetrical molecules from a position of more stable orientation When heat is supplied to a body from without it raises the temperature if it increases the molecular kinetic energy, it may, on the other hand, pass into the form of molecular potential energy, in which event it constitutes latent heat For example, the 'latent heat of expansion' of an imperfect gas, heated at constant pressure, represents the work done against the molecular attractions, latent heat of vaporisation represents mainly work done in removing the molecules to the great distance which separates them in the state of vapour Latent heat of fusion represents work done in displacing the molecules from their ordered arrangement in the space lattice of the solid to the completely random orientation which prevails in the liquid state the increase in potential energy which the actual de-orientation involves is increased or diminished by a term depending on the relative distances apart of the centres in the solid and the liquid states respectively

We have seen the important relation between temperature and the kinetic portion of the total energy It depends upon a very general theorem in mechanics, the principle of the equipartition of energy This principle determines the partition of kinetic energy among the various degrees of freedom in a system composed of a large number of bodies, such as molecules, all executing complex motions of translation, rotation, and vibration, and capable of transferring energy one to another The average kinetic energy is the same for each degree of freedom The average translational energy per molecule of a gas is the same, for the translational motion resolved along each of the three axes, as the average rotational kinetic energy about each of the possible axes of rotation Subject to certain restrictions introduced by the quantum theory these general mechanical results are confirmed completely by experiment

If we suppose two bodies to be placed in contact, energy will be transferred from one to the other (the simplest way is by molecular collisions at the boundary) until the average kinetic energy per molecule per degree of freedom is the same for each body They will then be in statistical equilibrium, and no further net passage of heat will take place This is precisely the criterion of temperature equality which empirical thermodynamics uses

The existence of a statistical equilibrium in respect of the molecular energies is the mechanical counterpart of the existence of an empirical temperature The fact that the actual mechanical law governing the statistical equilibrium is the equipartition principle leads to the direct proportionality of temperature and kinetic energy per degree of freedom The quantum theory introduces no real difficulty it is at most a practical difficulty, and even then we can always define the temperature of a solid body as equal to the temperature of the monatomic gas with which the body will come into thermal equilibrium The original kinetic conception of the temperature of a gas is unaffected by quantum modifications

Having recapitulated these general ideas, we may now proceed to consider more fully the molecular interpretation of the second law of thermodynamics and the physical meaning of entropy We have already seen the distinction between mass motion and molecular motion, and seen how the conversion of mechanical energy into heat entails the transformation of ordered mass motion into random molecular motion Let us consider a mass of gas at a temperature θ_1, and fix our attention on the individual molecules These are moving with different velocities in all directions To depict the state of the gas at any instant a series of lines can be drawn from some fixed origin to represent the velocities in magnitude and direction The lines vary in length, but the mean length is definitely determined by the value of θ_1 Their directions in space are absolutely random At the instant under consideration let the mass of gas as a whole be conceived to move in a given direction with velocity v This means that each individual molecule has now, in addition to its random motion of thermal agitation, a component v in a direction which is the same for all the molecules From the point of view of a single molecule this is of course indistinguishable from the ordinary thermal velocity and compounds with it to a single resultant This resultant velocity is modified by each collision which the molecule undergoes, and soon the common directed component v will no longer be distinguishable even when all the molecules are taken into consideration A new series of lines could now be drawn to represent the molecular velocities the directions would be random as in the original instance, but the average length would be greater than before The increase in the average length corresponds to the increase in the temperature to θ_2

The important point is the disappearance of the directed velocity component The velocity components have become mixed up as regards their distribution in space The distribution is said to be a more probable one than before The meaning of the word probable is made clearer when we say that the reverse process, namely, the cooling of the gas and its moving off as a whole is an improbable process in the same sense It is improbable that the common component originally possessed by all the molecules will ever emerge again from the chaos of molecular velocities This is simply the second law, which can be stated in the form that molecular configurations always tend to pass from a less probable to a more probable state Incidentally, we must notice that in the case just considered of the gas becoming hotter and losing its mass kinetic energy the entropy increases simultaneously with the probability of its condition Here we have the simplest instance of the correlation between the entropy of a system and the probability of its condition This is a correlation which we have to examine in some detail as it reveals the true significance of entropy The purely thermodynamical result that all spontaneously occurring processes are accompanied by an increase of entropy means that every system tends to pass from its existing state into a state where the mechanical condition of its molecules is a more probable one

We have just seen how a distribution of velocities can become more probable But the state even of a monatomic 'perfect' gas is not completely determined when only the magnitude and direction of the molecular velocities are known The positions in space of the molecules must also be known Positional co-ordinates and velocity co-ordinates are both necessary for defining the mechanical state of the gas When a gas expands to double its initial volume it passes into a more probable state The truth of this is evident if we reflect that only the most improbable series of collisions could result in the retreat of all the molecules into half the final volume, leaving the other half of the space vacuous If there were only a dozen molecules they might, by a not very improbable chance, collect themselves into one-half of the total space at their disposal But that the many millions of molecules which are contained in even the minutest bubble of gas should all do this would be an event of that transcendent degree of improbability which empirical thermodynamics calls impossibility.*

The two important things, then, are (*a*) a probable distribution of velocities, (*b*) a probable arrangement of the molecules in space The primitive form of the second law of thermodynamics, namely, that heat cannot pass spontaneously from a colder to a warmer body, follows from the first requirement For were this to happen the cold body would become colder and the hot body hotter The difference between the average velocities of the two sets of molecules, belonging respectively to the cold body and the hot body, would increase Instead of all the velocities merging into one indistinguishable group they would fall apart into two more and more widely differentiated sets This is an 'improbable' occurrence, or an event which is very much at variance with the laws of chance, just as though shuffling a pack of cards should sort them

We know, however, that heat can be made to pass from a body at a lower temperature to one at a higher, if at the same time work is performed on the system by some external agency For example, this happens when a Carnot cycle is driven backwards

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* When we speak of random molecular motion we must avoid the error of supposing that the motion of each molecule is not determined during all its subsequent history when the initial condition of the gas is known We only mean that at a given instant as many molecules are moving in one direction as in another The motion being determinate, but far too complex for us to calculate in detail, we cannot say that the gas will not at some time pass into a highly 'improbable' condition But we know that it will pass out of it again, and that during the whole of its existence it will spend but an infinitesimal fraction of its time in 'improbable' states

This brings us to the subject of thermodynamic ' compensation ' The meaning of this term may be recalled Heat cannot pass from a colder to a warmer body without ' compensation,' that is, without work being performed Heat cannot be converted into work without ' compensation,' which consists in some such change as the expansion of a gas, or the simultaneous passage of some heat from a hot body to a colder one as in the direct Carnot cycle In all these examples there is a change from a more probable to a less probable state, which would not occur by itself The ' compensation ' in each instance consists in an accompanying change from a less probable to a more probable state in some other respect In the compensation there is an increase in probability of condition which balances the decrease in probability attending the primary process

Suppose, for example, work is performed by the adiabatic expansion of a gas The kinetic energy of the gas molecules decreases A weight could be raised, which, in falling again, could impart mass kinetic energy to the gas itself Thus the gas cools and moves This is a passage to a less probable state But the gas now occupies a larger volume. The probability of the spatial distribution of its molecules has increased The probability of distribution of the molecular velocities has diminished The two things compensate for one another. It is noteworthy that a more probable distribution of molecules in space may make up for a less probable arrangement of velocities

In the Carnot cycle we have conversion of heat into work involving an analogous passage from a more probable to a less probable state The compensation consists in the simultaneous passage of some heat from the high temperature to the low temperature source. This is in effect equivalent to the equalisation of a temperature difference, a merging of two separate sets of molecular velocities into one indistinguishable set Here both the improbable event and the compensating event are concerned with the velocities, and not with the space co-ordinates, which are unaltered at the end of a complete cycle

At the end of all cyclic processes the space co-ordinates are unaltered, and any compensations have all to be concerned with the velocity co-ordinates

The two sorts of probability can be seen each to be represented by a term in the expression for the entropy of a perfect gas This expression is

$$S=C_v\, ln\ \theta+R\, ln\ v+\text{constant}$$

The matter becomes clearest when approached in the following way Consider two separate gram molecules of the same gas, one having temperature θ_1, and volume v_1, the other having temperature θ_2 and volume v_2 Let them be mixed, as by the turning of a tap, the total volume remaining constant The new entropy is

$$2\left\{C_v\ ln\,\frac{\theta_1+\theta_2}{2}+R\ ln\ (v_1+v_2)+\text{constant}\right\},$$

since we now have two gram molecules of gas occupying a volume v_1+v_2, and having a temperature $\frac{1}{2}(\theta_1+\theta_2)$

$2R\log(v_1+v_2)$ is clearly greater than $R\log v_1+R\log v_2$, and the excess represents the increase in entropy due to the mixing of the two lots of gas and the equalisation of pressure The connection of this term in the entropy expression with the probability of the spatial distribution of the molecules is thus obvious, since it is clearly more probable that the molecules shall be uniformly distributed throughout the whole volume than that they shall be more densely packed in one portion of the space and less densely in the other

With regard to the other term depending on θ,

$$2C_v\, ln\,\frac{\theta_1+\theta_2}{2}$$

is readily seen to be greater than $C_v\, ln\ \theta_1+C_v\, ln\ \theta_2$, for $ln\ \theta_1+ln\ \theta_2=ln\ (\theta_1\theta_2)$, while $2\ ln\ \frac{\theta_1+\theta_2}{2}=ln\left(\frac{\theta_1+\theta_2}{2}\right)^2$. θ being an essentially positive quantity, this last expression must, of course, be greater than $ln\ (\theta_1\theta_2)$ * Thus we see that there is an increase in the total entropy due to the equalisation of temperature After this equalisation the distribution of molecular velocities is also a more probable one, since the velocities are no longer divided into two separate groups

These considerations establish a general parallelism between the entropy of a system and the probability of its condition

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* $\left(\frac{\theta_1+\theta_2}{2}\right)^2=\frac{1}{4}(\theta_1^2+\theta_2)+\frac{1}{2}\theta_1\theta_2$ We have thus to show that $\frac{1}{4}(\theta_1^2+\theta_2^2)>\frac{1}{2}\theta_1\theta_2$ or $\theta_1^2+\theta_2^2-2\theta_1\theta_2>0$ This must be so as $(\theta_1-\theta_2)^2$ is positive

It now remains to seek a more precise connection A definite quantitative definition of probability of condition is first necessary There has been no difficulty in seeing qualitatively what is meant by the statement that a system passes from a less probable to a more probable state It means simply that the reversal of the process by which the change occurred would demand a series of molecular happenings against which the odds are very great Boltzmann put the whole matter in an exact quantitative form

For simplicity we confine our attention once more to a monatomic gas Let the number of molecules be N, the temperature θ, and the volume v Boltzmann regards the gas from two aspects, as a mechanical system on the one hand, and as a thermodynamical system on the other To define its condition in the first sense it is necessary to know at any instant six factors relating to each single molecule, namely, the three components of its velocity and the three co-ordinates fixing its position in space

Mechanically, the gas is in a state of perpetual change, the molecules move hither and thither, and at each collision their velocity changes, becoming now great and now small But to an observer unable to appreciate the vicissitudes of individual molecules the gas attains an apparently steady condition of uniform temperature and pressure, so long as it is free from external influences Thus, the knowledge of two quantities only, namely, temperature and pressure (or volume) may be said to define in it the thermodynamic sense. This is a much less refined analysis of the actual state of the molecules than is demanded by the mechanical definition, which involves the knowledge of $6N$ quantities

The pressure of the gas depends upon the number of molecules in each element of volume If we divide the whole volume up into elements dv, and denote the number of molecules in each by ndv, there will be a uniform pressure when n has the same value for each element The elements, although small, must be of sufficient size for n to be a large number For a given element of volume the actual individual molecules making up the ndv change continually Indeed, after the lapse of a short time the majority of the original ndv molecules will have been replaced by others But the total number ndv remains constant except for minor fluctuations which can be made as small as we please by choosing the size of dv suitably The gas is said to be in a steady state or in statistical equilibrium Now we come to the essential part of Boltzmann's interpretation The $n\,dv$ molecules in the volume element dv can be made up out of the N individuals in a great many different ways, just as from 100 identical objects five can be selected and placed in a box in $\dfrac{\underline{|100}}{\underline{|95}\;\underline{|5}}$ ways Let us suppose we wish to define the state of the gas with regard to its density at every point, this density being not necessarily a uniform one Let x, y, and z be the rectangular space co-ordinates fixing the position of the element dv We must then know n in terms of x, y, and z We may suppose that in successive volume elements dv_1, dv_2 there are respectively n_1dv_1, n_2dv_2, n_3dv_3 molecules The thermodynamic state of the gas is defined with regard to pressure if we can say in this way that there are n_1dv_1 molecules in dv_1, n_2dv_2 in dv_2, etc There are N molecules in all Now N things can be arranged in groups of a, b, c in $\dfrac{\underline{|N}}{\underline{|a}\;\underline{|b}\;\underline{|c}}$ ways Therefore there are

$$\frac{\underline{|N}}{\underline{|n_1dv_1}\;\underline{|n_2dv_2}\;\underline{|n_3dv_3}}$$

ways in which the actual molecules can fulfil the 'thermodynamic' condition

Analogous considerations apply to the molecular velocities Thermodynamically, we know all we require about the gas, if we can say that so many molecules have speeds between such and such limits, so many between such and such other limits, and so on It is a matter of indifference which individuals go to make up each little specified group

Thus we see that a given thermodynamic condition of the gas can be realised by a great many arrangements of the individual molecules The number of such arrangements Boltzmann calls the number of *complexions* The number of complexions is taken as a quantitative measure of the probability of the condition of the gas A little reflection will show why this is justified The conditions which will occur most readily in the gas are those which can be realised by the greatest number of molecular arrangements Returning for a moment to the expression for the number of arrangements of the molecules in the elements dv, etc, $\dfrac{\underline{|N}}{\underline{|n_1dv_1}\;\underline{|n_2dv_2}}$

we can take $dv_1=dv_2=dv_3$. , the gas, when left to itself, tends to assume a state fluctuating only to a very small extent on either side of that for which this number is a maximum. It is easy to satisfy oneself that a factorial expression of the form $\frac{|\underline{N}}{|\underline{a}\ |\underline{b}\ |\underline{c}}$, where $a+b+c\ .\ .\ .\ =N$, is greatest when $a=b=c$ In this case, then, the condition of maximum probability is reached when $n_1=n_2=n_3$, that is, when the density of the gas is uniform throughout

Although this result could easily enough have been foreseen without calculation, its derivation has served to illustrate Boltzmann's method in a simple way When we have to deal with the distribution of velocities the problem becomes more complicated If the velocity of a molecule is defined by the rectangular co-ordinates u, v, w, we have to consider how many molecules have velocities between u and $u+du$, v and $v+dv$, w and $w+dw$, or, imagining each velocity represented by a line, how many molecules have velocities represented by lines terminating in the element $du\ dv\ dw$. This may be expressed briefly by saying that we require to know the number of molecules in each velocity element $du\ dv\ dw$ We cannot conclude, as we did in the case of the spatial distribution, that the maximum number of arrangements of molecules for a given thermodynamic state is obtained when the numbers of molecules in each velocity element are equal, because while the actual total volume of the gas is finite, the volume of the three dimensional velocity diagram is infinite, and we have now another condition to fulfil, namely, that the total kinetic energy of the gas is constant Subject to this condition Boltzmann found the maximum number of arrangements or complexions to be greatest when all the gas has the same temperature, and when Maxwell's law of distribution applies

An expression for the number of complexions by which the thermodynamic state of a perfect gas is realised can be worked out in terms of θ and v Let this number be W

As we have already seen, there must be some connection between W and the entropy S A quite general argument gives an indication as to what function of W should be connected with S We write in the first place $S=f(W)$ Now we consider two gases for which the values of W are respectively W_1 and W_2, and the entropies of which are S_1 and S_2

The total entropy is S_1+S_2 If the first gas can realise its thermodynamic condition by W_1 molecular arrangements, and the second by W_2 independent arrangements, there are W_1 arrangements of the first for every one of the second, or W_1W_2 in all

W_1W_2 is the 'probability' of the composite system

Therefore $S=f(W_1W_2)$,

but $S=S_1+S_2=f(W_1)+f(W_2)$,

thus $f(W_1W_2)=f(W_1)+f(W_2)$

The function which satisfies this last relation is a logarithm Thus we see that we should seek a correlation between the entropy and the *logarithm* of the probability, and we write

$$S=\text{constant}\times ln\,W$$

Boltzmann finds the value of *ln* W for one gram molecule of a monatomic gas to be given by

$$ln\,W=N\,ln\,v+\tfrac{3}{2}N\,ln\,\theta+\text{constant},$$

but $S=R\,ln\,v+C_v\,ln\,\theta+\text{constant}$

and since $\dfrac{R}{N}=k$ and $C_v=\tfrac{3}{2}R$,

we have $S=k\,ln\,W$

Boltzmann's exact derivation of the expression for log W is too lengthy to be given here The complication of it arises largely from the fact that the molecules have velocities distributed in accordance with Maxwell's law The following simple derivation of the entropy formula of a monatomic gas from the laws of chance may help, however, to render the relation between entropy and probability clear

(1) Suppose a gas has expanded from volume v_1 to volume v_2 at constant temperature Let the smaller volume v_1 be imagined marked out in the larger volume The chance that a given molecule, free to move through the whole volume v_2, shall find itself within v_1 is $\dfrac{v_1}{v_2}$. The chance of its being somewhere in v_2 is greater, therefore, than its chance of being in v_1 in the ratio $\dfrac{v_2}{v_1}$ For two given molecules the chance becomes $\left(\dfrac{v_2}{v_1}\right)^2$ times greater, and for N molecules the chance is $\left(\dfrac{v_2}{v_1}\right)^N$ times greater

Thus $$\frac{W_2}{W_1}=\left(\frac{v_2}{v_1}\right)^N,$$

$$k\ ln\ \frac{W_2}{W_1}=kN\ ln\ \frac{v_2}{v_1},$$

thus $$k\ ln\ W_2-k\ ln\ W_1=kN\ ln\ v_2-kN\ ln\ v_1,$$

or, generally, $$k\ ln\ W=kN\ ln\ v+\text{constant},$$

but $$k=\frac{R}{N},$$

therefore $$k\ ln\ W=R\ ln\ v+\text{constant},$$

when θ is constant

(2) Now suppose the volume to remain constant

Let the temperature be θ_2 Let each velocity component have the average value u_2

Now suppose the gas drops in temperature to θ_1, each velocity component now having the average value u_1 Unless the probability of condition of some other body changes also, in which case we cannot draw conclusions without taking this other body into account, we must suppose that the heat which the gas loses is converted into directed motion In other words, each individual velocity develops a singularity which was absent before Each of the $3N$ quantities shrinks in effect from u_2 to u_1 The new state of the gas is less probable than the old in a ratio which may be represented by $\left(\frac{u_1}{u_2}\right)^{3N}$, for we may think of each of the $3N$ components being simultaneously changed in collision in such a way that only $\frac{u_1}{u_2}$ of it remains random motion Thus, we have

$$\frac{W_1}{W_2}=\left(\frac{u_1}{u_2}\right)^{3N},$$

but $$u_1=\text{constant}\ \sqrt{\theta_1}\ \text{and}\ u_2=\text{constant}\ \sqrt{\theta_2},$$

$$\frac{W_1}{W_2}=\left(\frac{\theta_1}{\theta_2}\right)^{\frac{3N}{2}},$$

$$ln\ W_1-ln\ W_2=\frac{3N}{2}\ ln\ \theta_1-\frac{3N}{2}\ ln\ \theta_2,$$

therefore $$ln\ W=\frac{3N}{2}\ ln\ \theta+\text{constant},$$

when the volume is constant.

$$k\,ln\,W=\frac{3kN}{2}\,ln\,\theta+\text{constant},$$

$$\frac{3kN}{2}=\frac{3R}{2}=C_v$$

Thus we have

$$k\,ln\,W=C_v\,ln\,\theta+\text{constant},$$

when v is constant ,

and $$k\,ln\,W=R\,ln\,v+\text{constant},$$

when θ is constant

Combining the two equations, we have

$$k\,ln\,W=C_v\,ln\,\theta+R\,ln\,v+\text{constant}$$

This is the same as the expression for S derived from the equation $dS=\frac{dQ}{\theta}$

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